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A TERTIARY-QUATERNARY PEDOLOGICAL CHRONOLOGY FOR THE SOUTH-EASTERN PORTION OF THE AUSTRALIAN ARID ZONE

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Summary

The alternation of pluvial and non-pluvial periods during the Tertiary-Quaternary resulted in periodicity of soil formation and landscape development. Soils were formed during the pluvial periods, when the landscape was protected from erosion deposition by a well-developed vegetative cover. Varying amounts of erosion and deposition occurred during the non-pluvial periods, when the vegetative cover was sparser.

The Tertiary erosional periods were characterized by water erosion-deposition and major changes of land form. During each of the Quaternary erosional periods the climate became desertic; there was widespread erosion by wind but little modification of the landscape.

The soils are of four different ages. In addition, surface silcretes were formed during another period of landscape stability. All of the soils in the region are paleosols.

Introduction

In a series of earlier papers (Jessup, 1960*a*, *b*, *c*, *d*; 1961*a*, *b*) the evolution of the soils in two extensive areas in the south-eastern portion of the Australian arid zone, beginning with the oldest surviving soils (laterites), was discussed. The purpose of this final paper is to present a pedological chronology for the region.

The Surfaces of Erosion

Remnants of two ancient surfaces of erosion form plateaux and mesas that, in most areas, rise abruptly above an extensive third surface of low relief (the youngest surface).

Remnants of the oldest surface form a series of high mesas between Port Augusta and Lake Torrens and the extensive Arcoona plateau which lies immediately to the west of Lake Torrens (Fig. 1). The surface slopes downwards from the coast towards the north; it descends from 1,100 ft. to 400 ft. above sea-level between Port Augusta and the northern boundary of the Arcoona plateau. Near Port Augusta the mesas rise 600–900 ft. above the surrounding plains while, along its northern and western boundaries, the Arcoona plateau dips under the plains of the youngest surface.

The mesas and the Arcoona plateau consist principally of Precambrian–Cambrian sandstones and quartzites, commonly 300 ft. thick, overlying shales (Segnit, 1939). These sediments are overlapped unconformably by Cretaceous deposits around the northern fringes of the Arcoona plateau. Erosion has subsequently destroyed the Cretaceous sediments in many places and exhumed the ancient surface on which

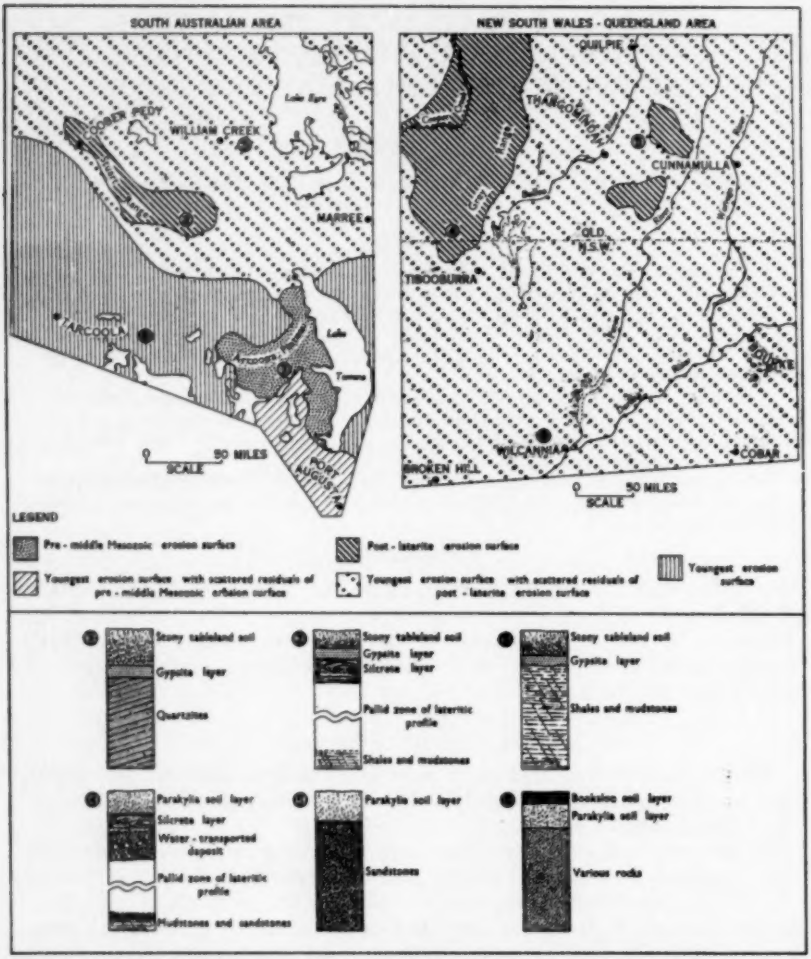

FIG. 1. The distribution of the erosion surfaces in the two areas studied and the occurrence of the soil layers at some representative sites.

they were deposited. This old surface is, therefore, of pre-middle Mesozoic age.

The sandstones and quartzites of the pre-middle Mesozoic surface are overlain by superficial layers, a few feet thick, consisting of materials unlike those in the rocks. In some localities a layer of fine-textured (clay) soil and an underlying layer of gypsite are superimposed upon the sandstones and quartzites. Elsewhere these rocks are overlain by a calcareous soil layer.

Scattered remnants of the second oldest surface (referred to below as the post-laterite erosion surface) are widespread (Fig. 1). They form plateaux and mesas that commonly rise 150 to 300 ft. above the plains of the youngest surface. The remnants are capped by a layer of silcrete several feet thick below which there are usually deposits of water-transported materials containing gravel and boulders. These deposits, which may be as much as 50 ft. thick, usually rest upon white kaolinite and soft white kaolinitic sandstones, but occasionally the upper part of the kaolinite and sandstones shows red and white mottling. These white materials extend to the base of the escarpments. The silcrete capping on the remnants of the post-laterite erosion surface is overlain by superficial layers like those on the pre-middle Mesozoic surface remnants.

The extensive youngest erosion surface (see Fig. 1), which forms the vast plain above which the remnants of the two older surfaces rise, was cut either in the lower part of the kaolinized materials or unweathered rocks that occur below them. The superficial layers that occur on the remnants of the pre-middle Mesozoic and post-laterite surfaces are present on this youngest surface.

The remnants of the pre-middle Mesozoic surface were already in existence by the beginning of the Tertiary and, except for the origin of the soil and gypsite layers on them, are not further discussed in this paper.

Dissection of the post-laterite erosion surface (Fig. 2 (2)) resulted from drainage rejuvenation that followed continental uplift and down-sagging of the Lake Eyre basin in the Miocene (King, 1950; Twidale, 1956). Uplift was apparently uneven and was greatest around the margin of the Lake Eyre basin, where a divide separating oceanic from interior drainage was created. Along the divide, as in the Stuart Range, the post-laterite erosion surface is elevated 750–850 ft. above sea-level.

The extensive youngest surface (Fig. 2 (4)) developed following the cessation of the earth movements. In the vicinity of the divide between oceanic and interior drainage this younger erosional plain was cut in the lower part of the kaolinized materials. Away from the divide the difference in height between the post-laterite and the youngest surface is greater, and here the latter was cut in unweathered rocks. Erosion was accompanied by extensive sedimentation in the Lake Eyre basin (Glaessner, Parkin *et al.*, 1958), the lower part of which was occupied by the vast Lake Dieri. Lake Eyre itself did not exist at this time (see below).

Tertiary Pedological History

The sequence and origin of the materials exposed in the escarpments of the remnants of the post-laterite surface have been discussed by Jessup (1960*b*). It was shown that the mottled and white kaolinized layers are horizons of a truncated lateritic profile (the mottled and pallid zones respectively). While the ferruginous zone, as well as the mottled and pallid zones, have survived in other parts of Australia, for example, in parts of Western Australia (Jutson, 1934), the Northern Territory (Stewart, 1956), and Queensland (Whitehouse, 1940), in the areas studied

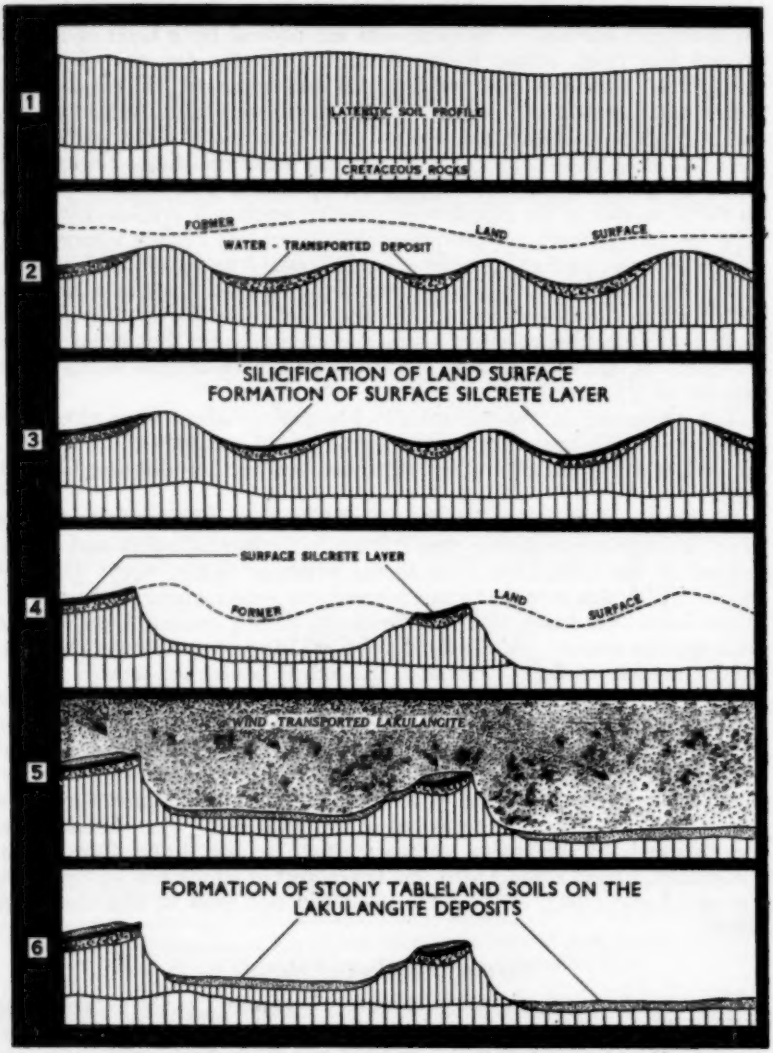

FIG. 2. Diagram illustrating the Tertiary and earlier Quaternary pedological and geomorphological history of the south-eastern portion of the Australian arid zone.

the upper part of the lateritic profile was everywhere stripped off during the formation of the post-laterite surface. Thus there are no remnants of the actual land surface (Fig. 2 (1)) on which the lateritic soil developed. Water-transported deposits, that consist of detritus stripped from the lateritic profile in adjacent sites, overlie the mottled or pallid zones. The layer of silcrete that caps the residuals of the post-laterite surface was formed as a result of the subsequent cementation, by silica, of the upper part of the detrital deposits (Fig. 2 (3)).

The youngest rocks on which the lateritic profile developed are of Cretaceous age, while Glaessner, Parkin *et al.* (1958) have ascribed an earlier Tertiary age to the deposits that were laid down when the lateritic profile was truncated. The time of formation of the lateritic profile and of the silcrete layer can now be approximately established. They both formed during the early to middle Tertiary. The lateritic soil developed after the emergence of the region from beneath the Cretaceous seas and lakes and prior to the erosional period of the earlier Tertiary, when it was truncated. The silcrete layer formed after the earlier Tertiary deposits were laid down and prior to the Miocene earth movements that led to dissection of the silcrete-capped land surface.

There has previously been considerable controversy regarding the age of the lateritic soil. It has been suggested that it formed during the Pliocene (Bryan, 1939; Whitehouse, 1940), throughout the period Cretaceous to Pliocene (King, 1950) and in the early to middle Tertiary (Twidale, 1956).

The nature of the climate, during part of the early to middle Tertiary, can be inferred from the presence of the lateritic soil and silcrete layer. Deep lateritic soils form under conditions of high rainfall and high temperature (D'Hoore, 1954). In South Africa a humid climate with alternating wet and dry seasons is considered to have prevailed when surface silcretes developed (Frankel and Kent, 1938). The Australian silcretes probably formed under comparable conditions since 'any valid hypothesis of the mechanism of silcrete formation in South Africa will probably also apply to Australian occurrences' (Williamson, 1957).

Quaternary Pedological History

Sedimentation in the vast internal drainage basin continued from the late Tertiary into the Quaternary period. During this prolonged period of erosion-deposition the climate became progressively drier and finally Lake Dieri dried out. The youngest lacustrine sediments, which consist of a highly gypseous bed overlying clays, have been tentatively assigned to the early Recent (David and Browne, 1950; King, 1956). Jessup (1960*c*) has shown that fine-textured wind-borne materials (for which the term lakulangite was used), derived through deflation of the lacustrine sediments, were then deposited over a wide area (Fig. 2 (5)). The exposed gypseous bed was first deflated and a layer of wind-blown gypsite was laid down. This was followed by the deposition of a layer of wind-blown clay.

Wind-excavated hollows formed within the lacustrine sediments as a result of removal of materials by wind. The present playa lakes, the

largest of which is Lake Eyre, occur in these hollows (King, 1956; Jessup, 1960*c*).

The climate then became humid and lakulangite was no longer deposited. During this humid period soil formation took place. Stony tableland soils developed on the clayey lakulangite deposits (Jessup, 1960*c*). Because their parent materials were wind-blown clays, these fine-textured soils occur even on the highest features in the landscape (Fig. 2 (6)).

There was then a renewal of limited drainage incision and of surface stripping. Incision was probably induced by further tilting about the Lake Eyre basin (Mabbutt, priv. comm.). The stony tableland soil layer was destroyed in many areas in some parts of which a shallow fluviatile deposit, for which the name Curracunya has been used (Jessup, 1961*a*), was laid down.

After the stony tableland soil layer was eroded and the Curracunya deposit was laid down, a new soil layer was formed. This soil layer, for which the name Parakylia layer has been used, was discussed by Jessup (1960*d*, 1961*a*). It was shown that two distinct stages were involved in the formation of the Parakylia soil layer. These were an early period of erosion-deposition, when the parent materials were deposited, and a later period when the soils developed (Fig. 3). The parent material layer consisted of a mixture of wind-borne materials and locally derived water-transported ones. The wind-borne materials, calcareous clays, were eroded from calcareous soils on the Nullarbor Plain which lies to the west of the region. Wind-borne materials of this kind, namely those derived through deflation of soils, have been called parna (Butler, 1956). Erosion by wind followed the development of a sparse vegetative cover, due to the onset of arid climatic conditions. The soils formed following a change to wetter climatic conditions. Erosion-deposition was then at a minimum, the landscape being stabilized by a well-developed vegetative cover.

Parna was not trapped on the stony tableland soils which, in most areas, have been exposed at the surface of the landscape ever since they were formed, but it accumulated wherever these older soils had been destroyed. In addition to directly overlying the Curracunya fluviatile deposit and a variety of rocks on the youngest surface, the Parakylia layer occasionally overlies the sandstones and quartzites of the pre-middle Mesozoic surface residuals and the silcrete layer that caps the post-laterite erosion surface residuals.

While the depositional layer on which the Parakylia soils developed was highly calcareous, the Curracunya deposit is non-calcareous. Thus the nature, as well as the origin, of the materials in these two depositional layers differed markedly. The Curracunya deposit is highly indurated, probably because of siliceous cementation, and is separated from the overlying layer by a very sharp boundary. This difference in properties suggests it is unlikely that the two depositional layers were laid down during a single period of erosion-deposition. Furthermore, the Parakylia layer sometimes fills erosion gullies that were carved in the Curracunya deposit, that is, the two layers are separated by an erosional break. Thus

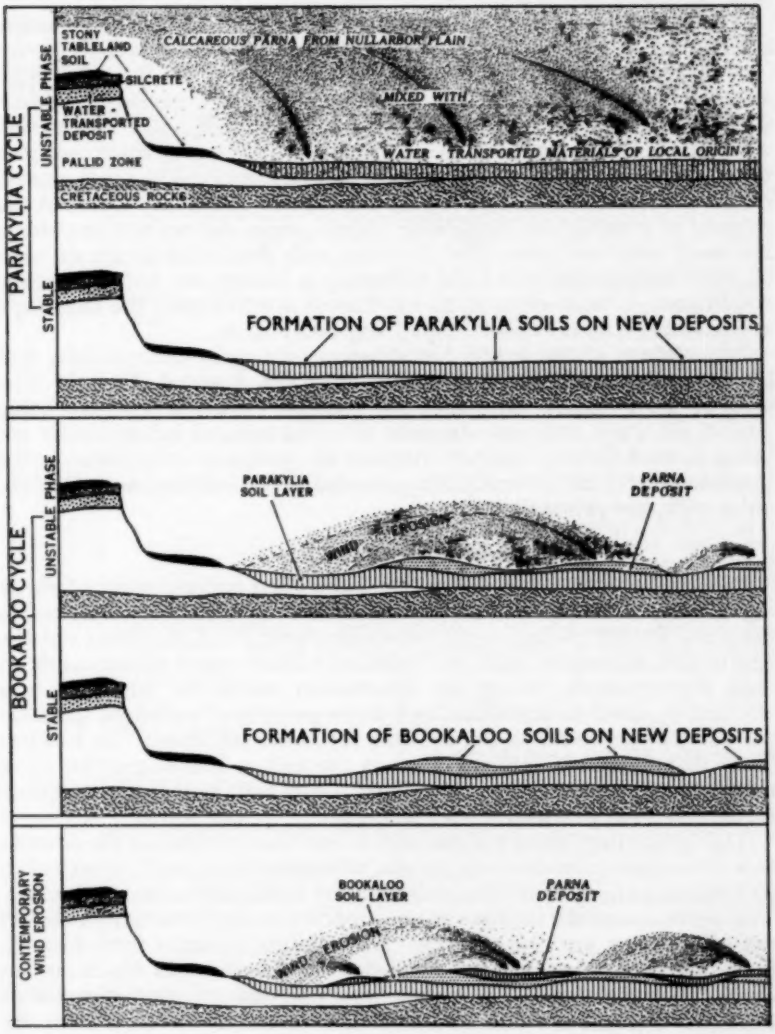

FIG. 3. Diagram illustrating the later Quaternary pedological history of the south-eastern portion of the Australian arid zone.

a considerable interval of time may have elapsed after the Curracunya deposit was laid down and prior to the deposition of the parent material layer of the Parakylia soils.

The Parakylia soil layer is, in turn, overlain by a discontinuous younger soil layer. This younger (Bookaloo) layer has been discussed by Jessup (1960*d*, 1961*b*). It was shown that the evolution of the Bookaloo layer also involved two distinct stages. These were an early period of erosion-deposition, when the parent materials were deposited, and a later period when the soils developed (Fig. 3). The parent material layer consisted of wind-transported materials (parna) that were derived through erosion of the soils in the Parakylia layer. Landscape instability followed the renewal of arid climatic conditions. Again, parna did not accumulate on the stony tableland soils. The Bookaloo soils developed on the deposits of wind-transported materials following a change to wetter climatic conditions. Erosion-deposition was then at a minimum; the landscape was stabilized by a well-developed vegetative cover.

The climate of the region has subsequently again become drier and a new period of landscape instability has been initiated (Fig. 3). The soils in the Bookaloo layer and the exposed Parakylia soils are being eroded by wind and new deposits of wind-transported materials are being formed (Jessup, 1960*a*). As even the youngest soils (those in the Bookaloo layer) are currently being eroded or buried they, as well as the older soils, are paleosols.

Conclusions

Previous workers have shown that Lake Dieri became extinct following the deposition of sediments that have been tentatively assigned to the early Recent (King, 1956). However, after the Lake dried out the region had a complex history (Table 1). There were subsequently at least three periods during the Quaternary when the landscape was affected by erosion-deposition and three periods of sufficient duration for soils to be formed on the deposits that were laid down. As it is unlikely that there was sufficient time in the mid to late Recent for all of these events to have taken place, Lake Dieri may have become extinct earlier than has previously been thought.

The Quaternary history of the region was characterized by the alternation of unstable (non-pluvial) periods, when erosion-deposition occurred, and pluvial periods when the landscape was stable and soils were formed. The landscape of the region was not modified to any great extent during the Quaternary unstable periods. Some minor features were formed, including sand-ridges and the wind-excavated hollows in which certain of the playa lakes occur. In addition, layers of wind-transported materials were laid down, but these were not of sufficient thickness to alter the general appearance of the landscape.

In contrast, there was major landscape-sculpturing during each of the Tertiary unstable periods. Furthermore, these periods were characterized solely by water erosion-deposition.

Like the Quaternary, the Tertiary was also characterized by the alternation of periods of stable and unstable landscape conditions. The first

TABLE I

The Climatic Régimes and Pedological History of the Tertiary-Quarternary

Tentative time scale	*Climate*	*Events*
Tertiary	Sub-tropical—high rainfall, high temperature (pluvial)	Formation of lateritic soils. Stable landscape.
	Semi-arid—intermittent torrential rainfall (non-pluvial)	Major water erosion-deposition. Truncation of lateritic profile. Post-laterite erosion surface formed.
	Humid—alternating wet and dry seasons (pluvial)	Formation of surface silcrete layer. Stable landscape.
	Progressive increase in aridity and finally desertic (non-pluvial)	Major water erosion-deposition. Sedimentation in Lake Dieri. Youngest erosion surface formed.
		Lake Dieri dried out. Deflation of the lacustrine sediments and widespread deposition of wind-blown materials (lakulangite).
	Wetter (pluvial)	Cessation of accessions of lakulangite. Stony tableland soils formed on the lakulangite deposits. Stable landscape.
Quaternary	?	Renewal of drainage incision. Stony tableland soil layer destroyed in many areas and Curracunya fluviatile deposit laid down. There followed an interval of time during which other events may have taken place.
	Progressive increase in aridity until finally desertic throughout almost whole of region (non-pluvial)	Deposits of wind-transported materials (parna), derived through deflation of soil lying to the west, laid down. The parna was mixed with water-transported materials (sands, gravel, &c.) of local origin.
	Wetter (pluvial)	Formation of (Parakylia) soils on the deposits of wind- and water-transported materials. Landscape stable.
	Arid throughout much of region (non-pluvial)	Parakylia soils eroded by wind in arid zone. New parna deposits laid down.
	Wetter (pluvial)	Formation of (Bookaloo) soils on the new parna deposits. Landscape stable.
Present	Arid throughout much of region (non-pluvial)	Wind erosion of Bookaloo and Parakylia soils in arid zone. New parna deposits being formed.

Tertiary erosional period was preceded by the period when the lateritic soil developed and the second by the period of silcrete formation (Table I). The lateritic soil profile, which was of great depth, could only have developed if the rate of soil formation exceeded that of erosion-deposition. Since soil formation proceeds at a slow rate erosion-deposition must have been at a minimum, that is, formation of the lateritic profile must have occurred during a period of landscape stability. The silcrete layer was formed as a result of the cementation, by silica, of the

upper portion of the deposits that were laid down during the first Tertiary erosional period. Thus the silcrete developed following the cessation of erosion-deposition when the landscape was stable.

A new erosion surface was formed during each of the Tertiary unstable periods. Earth movements, which caused renewed drainage incision, preceded the formation of each new surface. Renewed drainage incision may have resulted in unstable conditions on the steepened slopes adjacent to the drainage lines. However, erosion was not confined to these slopes.

During the first Tertiary erosional period the upper part of the lateritic profile was universally stripped off and as a result the pallid, or occasionally the mottled, zone was exposed. A gently rolling surface of erosion was formed. Water-transported deposits, consisting of detritus stripped from the lateritic profile in adjacent areas, accumulated on the gentle slopes between the drainage lines as well as in the valleys. In valleys and on slopes alike, the deposits are unsorted; gravel and large boulders are mixed with finer fractions. It is, therefore, evident that the materials were not transported far from their source, that mass-movement was involved, and that the landscape as a whole became unstable.

The kind of climate that prevailed during this erosional period can be inferred from the nature of the deposits and the process involved in their formation. Transportation of the erosional detritus was particularly inefficient. Inefficiency of transportation is a feature of semi-arid areas (Barrell, 1908). Sometimes layers and lenses of stones alternate with finer materials in the deposits indicating, as Whitehouse (1940) pointed out, that deposition occurred under conditions of intermittent torrential rainfall.

On the other hand, the climate prior to this erosional period must have been much wetter, since the deep lateritic soil was then formed. For the formation of such soils a sub-tropical climate with high rainfall and high temperature is necessary (D'Hoore, 1954). The onset of the erosional period was, therefore, associated with a change to drier climatic conditions.

The landscape would have been protected by a well-developed vegetative cover when the lateritic profile was formed, since the climate was sub-tropical. In contrast, there would have been a relatively sparse vegetative cover during the subsequent erosional period, when the climate was semi-arid. It is generally accepted that a dense vegetative cover reduces erosion to a minimum while a sparse cover is conducive to unstable conditions of landscape. Thus the change from landscape stability and soil formation to marked landscape instability was due to a decline in the density of the vegetative cover following the change to drier climatic conditions.

Mass-movement of materials could not have occurred on this gently rolling surface if there had been a well-developed vegetative cover. In the absence of man's activities, universal depletion of the vegetative cover over such large areas can only have resulted from an adverse climatic change.

There is also evidence of climatic change between the later stable and unstable periods of the Tertiary. Formation of the silcrete layer probably required a humid climate with alternating wet and dry seasons (Frankel and Kent, 1938). As already indicated, the erosional period that followed the formation of the silcrete was characterized by progressively increasing aridity.

As the erosional periods were initiated by a climatic change, the onset of general landscape instability and of planation did not necessarily directly follow the earth movements that caused renewed drainage incision. Tricart and Cailleux (1952) have also proposed that planation surfaces could not develop in areas with a dense vegetative cover and that Tertiary planations were climatically induced.

Discussion

It was previously generally accepted that, in Australia, the earlier Quaternary was characterized by humid climatic conditions (Table 2). The presence of extinct Pleistocene rivers and lakes and fossils of large herbivores in the arid interior was used as evidence that these conditions extended throughout the whole Continent (Tate, 1879, 1884). It was also generally considered that there was a period of major aridity during the later Quaternary and that this arid period was followed by a wetter interval and later by a return to drier conditions (Table 2).

However, Hills (1939), Gill (1955), Butler (1958), and van Dijk (1958, 1959) demonstrated that there were several arid periods during the Quaternary. Although Crocker (1946) and Stephens (1958) recognized that Quaternary climates influenced the genesis of some Australian soils, it has only recently been shown that Quaternary climatic changes resulted in periodicity of soil formation (Butler, 1958; van Dijk, 1958, 1959).

The Tertiary-Quaternary climatic chronology of the south-eastern portion of the Australian arid zone is summarized in Table 1. There were at least three cycles, each of which consisted of a desertic (non-pluvial) and a wetter (pluvial) period, in this region during the Quaternary. Furthermore, the conclusion of Whitehouse (1940), Tindale (1947), and Gill (1955) that the present climate is drier than that of the immediate past has been confirmed.

Previous workers (Beadle, 1948; Ratcliffe, 1936, 1937) attributed the widespread occurrence of truncated (eroded) soils in arid Australia solely to the period of contemporary wind erosion. However, the soils in the Parakylia layer were severely eroded in many areas during the earlier (Bookaloo) erosional period.

During the Quaternary there were a number of climatic cycles, each involving pluvial and non-pluvial periods, in many regions that are now desertic (Hack, 1942; van Riet Lowe, 1952; Hinds, 1952; Flint, 1959; Butzer, 1959). This has largely been deduced from studies of fluviatile deposits and changing lake levels. Wayland (1935) recognized that climatic changes in Uganda were responsible for periodicity of landscape evolution, that is, the alternation of periods of stable and unstable landscape conditions. Although they do not mention landscape periodicity, other workers (e.g. Gautier, 1926; Cotton, 1942, p. 92) have ascribed the

TABLE 2

Post-Miocene Climatic Chronologies presented by Earlier Workers

Period	*Epoch*	*Hills (1939)*	*Whitehouse (1940)*	*Browne (1945)*	*Crocker and Wood (1947)*	*David and Browne (1950)*
Recent	Upper	Alternating wetter and drier intervals; present and immediate past relatively wet	Relatively dry	More or less as at present	Slight decrease in rainfall	Much as at present but rainfall formerly somewhat greater
					Slight increase in rainfall	
	Middle		Humid	Cooler and wetter	Arid	Relatively humid
	Lower	Arid	Less humid	Arid	Rainfall less than in upper Pleistocene	Arid
Pleistocene	Upper	Humid	Arid	Cold and wet	Humid	Warmer than present
						Humid
						Warmer than present?
						Humid
	Middle	Humid	Humid	Probably warmer and wetter than present	Humid	Much warmer than present
	Lower	Humid	Humid	Humid	Humid	Humid
						Warmer than present
Pliocene	..	..	Relatively dry	..	High rainfall, high temperature	..
			High rainfall, high temperature			
			Relatively dry			
			High rainfall, high temperature			

formation of some of the landscape features in arid areas to former wetter climates. In spite of evidence of climatic periodicity, periodicity of soil formation has generally not been recognized, although Durand (1959) has demonstrated the alternation of stable (soil forming) and unstable (erosional) periods in Algeria.

The present study has shown that Tertiary-Quaternary climatic periodicity in arid Australia resulted in periodicity of both landscape evolution and soil formation.

Furthermore, it is now evident that soil destruction and burial, not soil formation, take place during desertic periods because there is insufficient vegetation to provide the stable conditions of landscape necessary for soil formation. Thus the concept of the 'desert type of soil formation' as discussed by Nikiforoff (1937) is invalid. The differentiated soils, as distinct from deposits of wind- or water-transported materials, that occur in desertic regions must everywhere have been pre-formed during earlier wetter periods.

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LATERITE AT THE TYPE LOCALITY, ANGADIPURAM, KERALA, INDIA

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(WITH FOUR PLATES)

Summary

Laterite at the type locality, Angadipuram in south India, consists of a mottled, vermicular, and indurated horizon in a red-earth type of soil associated with gneiss. The soil profile also contains deeper horizons of mottled and pale coloured clays and has a ground-water table. The laterite is associated with a number of discrete land surfaces described in detail by Lake (1890).

MATERIAL referred to as laterite is prevalent in both tropical and temperate parts of Australia. Because there is considerable variation in the soil and other weathered materials to which the term is applied by different workers in various countries the opportunity was taken during a visit to India in September 1960, to make an examination of laterite at the recognized original type locality at Angadipuram in Kerala state. The base for the visit was at Coimbatore which entailed traversing the great gap in the Western Ghats to Palghat at the western portal and so gaining ready access to the Malabar Coast. Angadipuram was approached from Palghat via Perintalmanna and laterite was seen to be abundant in road cuttings and quarries along much of the route. The return to Coimbatore was made via Pattambi, Shoranur, and Ottapalam along the valley of the Ponnani river to Palghat. The larger part of this traverse was also through a landscape with widespread occurrences of laterite.

Fox (1936), in his quotations from Buchanan's descriptions of the material to which he gave the name laterite, makes it clear that Angadipuram is the type locality and, prior to writing his account, visited it and other localities where Buchanan had found laterite. On the occasion of the present visit the exposures examined comprised several quarries for cutting laterite blocks, two wells in the town, a railway cutting about 60 ft. deep a short distance south of the station, and a number of surface exposures including one at the rest house at Perintalmanna.

A quarry on a gently sloping site near Angadipuram railway station showed the deepest soil found on top of the laterite (see Plate I). The following profile description was recorded:

0–7″ Friable, sub-plastic loam of fine vesicular structure; dark red (2·5 YR 3/5 moist) in colour; containing moderate amounts of lateritic gravel; diffuse boundary.

7–24″ As above except for a slight difference in colour (2·5 YR 3/6 moist) and with rather more gravel.

24–68″ Massive layer of laterite fairly sharply defined on top; coarse vermicular structure; red and yellow colours and with light grey mottles increasing with depth; not soft enough anywhere in the horizon to be cut with a knife,

but, except for the hardest upper few inches, being cut into blocks approximately 18″×9″×6″ with a broad-bladed pickaxe (see Plate II).

68″– Mottled clay exposure appearing in some of the deepest parts of the pit as an irregular and diffuse change from the hard laterite; strongly mottled reds (predominantly 10 R 3/4 moist), yellow-browns (predominantly 7·5 YR 5/6 moist), and light grey colours.

All horizons in the above profile contain a noticeable amount of quartz gravel greater than 2 mm. in diameter. In a laterite block forming part of the ascent to a temple west of the railway a large piece of fractured quartz about 6 in. across was observed.

Another profile in a pit about two miles west of Angadipuram consisted of about 10 in. of a red friable sub-plastic loam to clay-loam overlying 7–8 ft. of massive laterite below which the softer mottled clay showed the following moist colours: 7·5 R 4/8 and 5/8, 7·5 YR 4/4 and 5/8, and 2·5 Y 8/1. In this and nearby pits, the full depth of the laterite was being cut into blocks (see Plate III). Much more cellular and vermicular forms of laterite were seen in this locality and occasionally there were patches of black in the mottling of the material. Where the laterite outcropped on the surface, as in the exposure at the Perintalmanna rest house, it was much more uniformly dark in colour and rock-like in hardness or broken into a brown gravel of hard concretionary pieces which were very variable in size.

In the town wells and the railway cutting the mottled clay and the deeper situated 'pallid zone' were exposed. The latter was characterized by the absence of red colours, but some pale yellows and browns persisted in the nearly white matrix of soft clay and weathered rock. However, in the railway cutting the pallid zone clay rested abruptly on unweathered gneiss. This unexpectedly abrupt junction had also been noted by Fox. The water-table was well up in the mottled zone and discharged freely over the cut surface of the pallid zone and several feet of exposed rock into the drains alongside the railway track. In one of the wells the water-table appeared to be in the pallid zone but may have been low because of the normal draw on the well. The spoil from the other well showed gneiss in various degrees of weathering and kaolinization: vermicular laterite, mottled and pallid zone materials all retained some evidence of rock structure.

The landscape on which the laterite occurred proved to be a series of distinctly recognizable surfaces. Fox had noted the occurrence of laterite at different levels, e.g. at Perintalmanna about 450 ft. difference in elevation between laterite on top of a hill and that in the town, and writes of 'obvious differences in age and maturity of laterites'. He also remarks on *in situ* and detrital forms, the latter being reconsolidated. The geomorphic features of the Angadipuram landscape are illustrated in Plate IV which was taken from the hill-top temple mentioned previously. The highest feature shown is a foothill spur of the Western Ghats, the two flat-topped hills are remnants of a peneplain capped with laterite, the lower dissected hills are the remnants of a lower surface characterized by soils containing laterite on both crests and slopes and is the surface on which Angadipuram rests. The youngest surface shown

is occupied by the paddy fields, but it was not possible to be certain whether this was lateritic or not. However, some of the paddy fields in the district, such as at Pattambi, are constructed on lateritic terrain. This is also illustrated by some of Fox's photographs. It is thus clear that laterite has been formed on a discrete series of surfaces and therefore is of variable age. The lowest surface must be quite young and in fact possibly belongs to the present era.

Although Fox mentioned reconsolidated detrital laterite, none was recognized by the author as being similar to that studied in Australia and verified by thin section techniques (Stephens, 1946). Rather the impression was formed that the laterite occurring on the slopes of the small laterite-capped hills of the Angadipuram dissected surface had been formed *in situ* during or subsequent to the development of the slopes and could be classed as an absolute accumulation such as that defined by D'Hoore (1954) for African conditions where laterally moving groundwater has been responsible for development of the laterite in such situations.

Almost fifty years previous to Fox's visit Lake (1890) had described the distribution and nature of laterite over about 1,000 square miles of country around Angadipuram. The landscape sections presented in this most important paper make it clear that laterite occurs not only on a series of peneplain and terrace surfaces but also on slopes connecting these and on undulating terrain with a surface amplitude of the order of 100 ft. In fact despite its inadequate title in which no reference to laterite is made and which probably caused it to be largely overlooked this paper has a special significance today because of the steadily growing interest in the geomorphic relationships of laterite.

Lake classified laterite as follows:

1. Plateau laterite: almost always vesicular (vermicular) but may be mixed with a pellety type.
2. Terrace laterite: generally pellety (distinguished from pisolitic type of east coast).
3. Valley laterite: both pellety and vesicular types.

Massive and laminated forms are also mentioned. He describes laterite as a weathering product sedentary on gneiss and on transported materials, and in detrital and talus forms. He summarizes most interestingly: 'Speaking generally, laterite in Malabar has been formed by the decomposition of gneiss and the partial rearrangement by the mechanical action of water of the resulting materials. In other words *it is really a soil*.'

Because secondary siliceous materials are sometimes found in lateritic profiles in Australia a close watch was kept for similar materials, but none was encountered. However, Fox records a case 'where lithomarge (i.e. mottled zone) was especially siliceous', and members of the Indian Soil Survey in New Delhi remarked that they had occasionally encountered siliceous materials other than quartz in lateritic profiles.

From the observations made in the Angadipuram district and briefly recorded above it is apparent that the word laterite should be restricted to the particular material described by Buchanan and Fox and not ex-

A soil profile containing laterite exposed in a pit on a gentle slope a short distance east of Angadipuram railway station. The black handle of the knife in the centre is slightly more than 3 in. long.

C. G. STEPHENS—PLATE I

Laterite blocks being cut from the lower part of the laterite horizon in the pit near Angadipuram railway station.

C. G. STEPHENS—PLATE II

Laterite blocks stacked to harden after being cut from pits about two miles west of Angadipuram. On the right-hand side of the photograph it will be seen that the top of the laterite horizon just below the shallow soil is being cut into blocks.

C. G. STEPHENS—PLATE III

Part of the Angadipuram landscape as seen looking northwards from a temple west of the railway line. *A* is a foothill spur of the Western Ghats, *B* consists of two parts of the upper laterite-capped surface, *C* is composed of a lower dissected land surface containing laterite on both the tops and slopes of the small hills, *D* shows paddy fields on the lowest surface, and *E* is the river.

C. G. STEPHENS—PLATE IV

tended either to soft soil or other weathered materials or to whole profiles of earthy consistence; and that the adjectival form, lateritic, should be applied only to materials such as soil profiles which contain a recognizable horizon of laterite. There appears to be no case whatever for the neologism *latosol* which is antiphrastic as coined and used to describe deep soil profiles composed of red to yellow flocculated and friable clays of great permeability and with no ground-water or typically dense laterite horizon in the profile.

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SOME SARAWAK SOILS

II. SOILS OF THE BINTULU COASTAL AREA

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(WITH TWO PLATES)

Summary

The sub-mature landscape of the country rock (Miocene fine sandstones and shales) along the coast north of Bintulu gives rise under a mean annual rainfall of 150 in. to highly leached yellow soils, comparable to Kellogg's Red-Yellow Latosols, associated with lowland Dipterocarp rain forest. Areas of level or nearly level coarse-textured marine or estuarine deposits marking successive stages of the fall in sea-level during the Pleistocene are associated with ground-water podzols supporting various forms of the characteristic *kerangas* forest, which give rise to 'blackwater' streams.

PROFILES of soils in the coastal strip, 30 miles long and 5 miles deep, to the north of Bintulu (3° 10′ N., 113° 2′ E.) in Sarawak, Borneo, were recorded by one of us (T.W.W.W.) during a tour of duty in the area and on a further visit after a period of study leave in Oxford. The annual rainfall at Bintulu is 130–80 in. and there is no marked dry season, though in some years there may be a month in spring with as little as 3–4 in. of rain. Atmospheric humidity is almost consistently high, falling to perhaps 65–70 per cent. during the day, and remaining near saturation from dusk until the heavy morning mists are dispelled by the sun and offshore winds. There are constant heavy dews. The diurnal range of temperature may reach 18° F.; monthly mean temperatures are even throughout the year (Table 1).

TABLE 1

Meteorological Data for Bintulu, Sarawak (1953–8)

	Jan.	*Feb.*	*Mar.*	*Apr.*	*May*	*June*	*July*	*Aug.*	*Sept.*	*Oct.*	*Nov.*	*Dec.*
Mean monthly rainfall (in.)	15·7	14·1	8·1	8·1	7·2	10·9	10·7	10·7	13·9	15·9	14·5	19·1
Mean air temp. (°F.)	79·9	79·6	80·5	81·3	81·2	81·1	80·9	80·9	80·7	80·5	80·3	80·2
Mean daily bright sunshine (hrs.)	5·0	5·7	5·9	6·9	6·8	6·1	6·6	6·1	5·5	5·8	5·5	5·4

The area described differs from much of the north and central Sarawak and Brunei coast in that it still exhibits a considerable amount of relief

above the 100-ft. contour (Fitch, 1953, fig. 5). Several erosion surfaces,[1] marked by scattered remnants of beach sand and other alluvial deposits, indicate stages in the lowering of the sea-level during the Pleistocene.

Behind a series of low-level beach terraces, broken by low cliffs and rocky headlands, a gently undulating surface formed on the strongly to moderately folded fine sandstones and shales of the Setap (Miocene) group lies at 50–100 ft. above sea-level. The surface is dissected by steep-sided valleys several hundred feet wide and 40–60 ft. deep, still actively widening during the floods of the NE. monsoon. This belt is succeeded inland by a more deeply dissected landscape of crests and ridges rising to 100–200 ft., of which some are flat-topped or gently sloping, and possibly remnants of former flood plain surfaces, whereas others—narrow, steep-sided ridges often occurring in series—apparently represent outcrops of the more sandy facies of the country rock.

Following the end-Pleistocene rise in sea-level the rivers have filled their drowned valleys with mainly fine sandy or silty alluvium so that, for example, the Btg.[2] Kemena, the largest river in the district (Fig. 1), now flows in its lower reaches through a broad valley about 6 miles wide, in which freshwater swamp is ponded behind low sandy levées. The stage of development of the landscape appears to be that of early or youthful maturity (Kirk, 1957).

The greater part of the area is covered by lowland Dipterocarp forest. Second in extent and associated mainly with lighter-textured soils is *kerangas*[3] forest. The two types are distinct and the boundary is usually clear. Each is associated with a characteristic range of soil profiles, and the boundaries between soil types are equally distinct (Plate I.2). Less extensive, but at present more actively exploited, are the freshwater swamp forest on oligotrophic peat (Browne, 1954; van Wijk, 1951), and riparian forest (*empran*) developed where riverain alluvial deposits are sufficiently raised above tidal influence to be well drained for most of the year. Both these forest types are limited to the valleys.

The population of the area is not large. Some Chinese and Malays are distributed along the main rivers. The other races, Ibans, Kayans, and Penans, live in long-houses on stilts among or near their fields wherever land suitable for farming (mainly the relatively fertile alluvial soils and the heavier facies of the sedentary soils) is accessible by even the smallest of streams. They follow a shifting hill-rice and secondary forest rotation or cultivate permanent coconut, rubber, vegetable, or pepper gardens. Only the Chinese, the most intensive cultivators, who concentrate on gardens and plantations rather than rice, crop the sandy soils, and that to only a slight extent, using their customary 'pig-vegetable cycle' (Browne, 1952). The sandy coastal flats are grazed by cattle.

[1] Slightly to the north, at Miri, there is evidence of three major erosion surfaces, at 260 ft., 110–30 ft., and 35–40 ft. (Fitch, 1953), and in the Bintulu area there are at least two surfaces, at 30 ft. and 7 ft., represented by well-defined beach terraces and less well-defined stepped valley cross-sections (Kirk, 1957).

[2] Btg., Batang (large river); S., Sungai (river).

[3] From the Iban language: *kerangas* implies 'soil on which rice cannot be grown', and unlike the term *tanah karit*, unproductive soils (Blackburn and Baker, 1958), appears to be limited to soils of podzolic type.

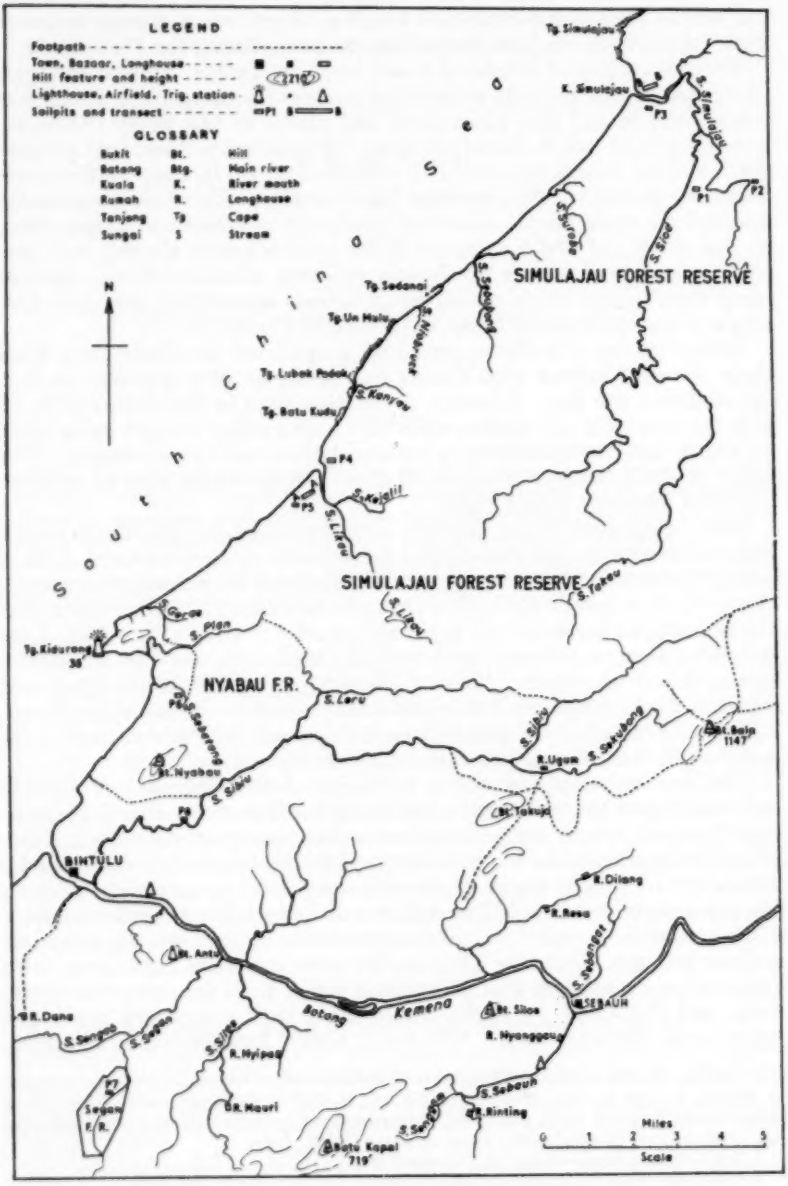

LEGEND
Footpath
Town, Bazaar, Longhouse
Hill feature and height
Lighthouse, Airfield, Trig. station
Soilpits and transect
GLOSSARY
Bukit Bt. Hill
Batang Btg. Main river
Kuala K. River mouth
Rumah R. Longhouse
Tanjong Tg Cape
Sungai S Stream
Tg. Simulajau
K. Simulajau
S. Simulajau
P1
P2
P3
S. Sarobe
S. Sisu
SIMULAJAU FOREST RESERVE
Tg. Sedanai
S. Sedanai
Tg. Un Hulu
S. Hilir Kerayu
Tg. Lubok Pedak
S. Kerayu
Tg. Batu Kudu
P4
P5
S. Kelalit
S. Likau
SIMULAJAU FOREST RESERVE
S. Tatau
S. Likau
S. Gerau
S. Pian
Tg. Kidurong
NYABAU F.R.
S. Laru
S. Sibiu
S. Sekubong
R. Ugum
Bt. Batu 1147
Bt. Nyabau
S. Sibiu
P6
S. Sekerang
Bt. Tokujo
BINTULU
R. Dilang
R. Rasa
S. Sekongei
Bt. Ante
R. Dana
S. Sengga
S. Sebu
S. Sibiu
Batang Kemena
Bt. Silos
SEBAUH
R. Hyangguang
R. Hyipan
P7
Sepan F.R.
R. Mauri
S. Sebauh
Bt. Rinting
S. Sengga
Batu Kapal 719'
Miles
0 1 2 3 4 5
Scale

FIG. 1

Soils beneath Empran Forest

The alluvial soils supporting *empran* forest[1] are considered to be the most fertile in the area. Profile No. 7 is typical.

Profile No. 7

Beneath *empran* forest 60 ft. from river on a 600-ft. belt of riparian flats beside the S. Segan 6 to 8 miles inland; 10–15 ft. above normal river level and subject only to seasonal flooding.

0–1″	Brown (10 YR 5/3)[2] very fine sandy loam; weak soft porous crumb; abundant fine roots and organic matter; sharp boundary to
1–9″	Yellowish-brown (10 YR 6/4) fine sandy loam, with faint pale yellow mottling; soft structureless; non-sticky, non-plastic; many fine roots, little humus discernible; merging into
9–18½″	Yellowish-brown (10 YR 6/4) fine sandy loam; no mottling; structureless; porous; many live roots; merging into
18½–26½″	Yellowish-brown (10 YR 5/4) fine sandy clay loam; slightly hard; structureless; some live roots, some visible organic matter; merging into
26½–36½″	Yellowish-brown (10 YR 6/4) fine sandy loam; finely fissured and porous; some live roots; merging into
36½–60″	Brownish-yellow (10 YR 6/6) fine sandy loam; with numerous faint yellowish mottles; porous and well fissured; non-sticky and non-plastic; some live roots; sand becomes coarser with depth.

At this site soils with similar profiles form a complex with sandy gley soils, in which the pale gley layer lies at 6 in. below a yellow surface horizon. The complex extends to the foot of the valley side, where it is succeeded by yellow sandy loam soils typical for the country rock.

Rooting is said to be much more extensive at all levels in such alluvial soils than it is in other soils of the area. For rice, at least, productivity is said to be highest on soils of heavy texture and optimum moisture régime—continuously wet but never flooded—a combination which occurs most frequently beneath *empran* forest. Such rice soils appear to correspond to soils of Class One (*tanah bakar*) and Class Two of the Brunei survey (Blackburn and Baker, 1958). They have been found at a few alluvial sites as above and on colluvial sites where moderately heavy shale-derived colluvium, together with bases derived from seeping ground water, provide comparable conditions. A composite sample (0–36 in.) from Profile No. 7 showed the following contents of cation nutrients:

Exchangeable (NH_4OAc): Na 0·01; K 0·013; Mg 0·23; Ca 0·26 m.e./100 g.

Total: Na n.d.; K 2·56; Mg 11·7; Ca 7·55 m.e./100 g.

Soils beneath Lowland Dipterocarp Forest

This forest type, mainly associated with undulating or steeply dissected terrain, extends from sea-level to about 1,500 ft. (Richards, 1952).

[1] *Belian* (*Eusideroxylon swageri*) and *engkabang* (*Shorea seminis*), with *selunsor* (*Tristania* sp.) and *ensurai* (*Dipterocarpus oblongifolia*) along the river edge, are characteristic species.

[2] Munsell notations for moist soil.

The upper canopy level composed mainly of the Dipterocarpaceae, of which the *Shorea*, *Dipterocarpus*, and *Dryobalanops* genera are most common, stands at 90–120 ft., although many trees extend to 150 ft. Apart from tree seedlings, there is little ground vegetation. Leaf litter is sparse. Climbers (*Ficus* and *Calamus* spp.) are frequent and orchids can be found high in the tree crowns. 'Dense though it is, progress through the forest is not unduly slow. Pig and deer tracks along spurs and ridges are easily followed. After the glare of river and open country, the forest is cool and pleasantly shaded.' Several characteristic soil profiles were examined. Locally, the soils are called *tanah kuning* (yellow soil), *tanah padi* (rice soil), or *tanah bukit* (hill soil). For present purposes we have named them Yellow Loam soils. Profile No. 8 is typical of soils on the steeper relief of the country rock.

Profile No. 8

Under Dipterocarp forest on a 10–15° slope some 100 ft. above sea-level, 2 to 3 miles inland, ¼ mile west of right bank of S. Sibiu.

0–3″ Yellowish-brown (10 YR 5/4) fine sandy clay loam with a well-defined soft porous crumb structure; slightly sticky; slightly plastic; abundant live roots and visible organic matter; sharp boundary to

3–13″ Brownish-yellow (10 YR 6/6) fine sandy clay loam; structureless, breaking into poorly defined clods; porous and finely fissured; slightly hard; slightly sticky, slightly plastic; live roots but no visible organic matter; merging into

13–25″ Reddish-yellow (7·5 YR 6/8) fine sandy clay loam, otherwise as above; merging into

25–31″ Brownish-yellow (10 YR 6/6) fine sandy clay with well-defined orange yellow mottling; structureless; finely porous; hard; few live roots; merging into

31–48″ Yellow (10 YR 7/6) fine sandy clay with conspicuous red mottling (2·5 YR 4/6); structureless; finely porous; slightly hard; very infrequent live roots; merging into

48–72″ Reddish-yellow, gritty fine sandy clay loam (7·5 YR 7/6) with conspicuous red mottling (10 R 8/4), possibly associated with weathering fragments of the parent material; a few fine pores; no live roots.

72″+ As above; soil wetter and more plastic.

Soils with similar profiles continue down the slope to the edge of the riparian flats.

Profile No. 4, found on slightly more sandy parent material, showed signs of incipient podzolization. The yield of commercial tree species, mainly Dipterocarps, in the standing forest round the profile pit gave only 595 Hoppus feet/acre on enumeration.[1]

Profile No. 4

Under Dipterocarp forest half-way up a 15–20° slope; ½ mile inland from the coast and ½ mile NE. of estuary of S. Likau.

2–0″ Matted roots and humus.

0–2″ Grey (10 YR 5/3) humic very fine sand; slightly pink in appearance; soft porous coarse crumb; numerous roots; merging to

[1] Details in thesis, 'A Study of the Coastal Soils of Bintulu District, Sarawak', T. W. W. Wood, Imperial Forestry Institute, Oxford (1957).

2–4″ Light yellowish-brown (10 YR 6/4) humic fine sand; soft coarse crumb to cloddy structure; porous; numerous live roots; moderate organic content; sharp boundary to

4–16″ 'Bright pale yellow fine sand; numerous roots';[1] merging to

16–34″ 'Stiff fine sand with slight pale mottling and numerous fine roots';[1] merging to

34″ Reddish-yellow (7·5 YR 7/8) fine sandy clay loam with conspicuous red (2·5 YR 5/8) mottles; structureless; porous; slightly hard to very hard; slightly plastic, slightly sticky; a few roots.

Below this depth mottling becomes more pronounced but no visible fragments of rock were encountered down to 60 in.

Profile No. 1 appeared to lie on a mid-slope terrace of riverain alluvium.

Profile No. 1

Under Dipterocarp forest 3 miles from the sea, on a raised terrace, 50 ft. wide, on the west bank of the S. Simulajau 2 miles from its junction with the S. Siod.

0–2″ Brown (10 YR 5/3 dry) fine sand with well-developed crumb; non-sticky and non-plastic; fair amount of humus and numerous live roots; sharp boundary to

2–8″ Yellowish-brown (10 YR 5/6) fine sandy clay loam; massive structureless; porous; slightly sticky, slightly plastic; some humus and some live roots; merging to

8–24″ Brownish-yellow (10 YR 6/8) fine sandy clay loam faintly mottled with small spots of grey, white, and red; very hard, poorly defined clods; sticky and plastic; distinctly porous and well fissured; a few live roots; no visible humus; merging to

24–48″ Brownish-yellow (10 YR 6/6) fine sandy clay loam with more conspicuous mottling than above; structureless; very hard; slightly sticky and slighty plastic; a very few live roots; sharp boundary to

48″+ Dark grey (5 Y 4/1) layered woody peat, with single grained fine sand; no live roots.

Yellow loam soils cover most of the ridge between the S. Simulajau and S. Siod, and are rather heavier in texture on the ridge than in Profile No. 1. Enumeration gave a total of 1,330 Hoppus feet/acre of commercial tree species round the profile pit.

The absence of discrete iron concretions in these profiles, except as partially indurated fragments of incompletely decomposed parent material, is characteristic for the region and has been commented on by Mohr (1944, p. 391).

Analyses of Profile No. 8 are given in Tables 2 and 3. The soil is acid throughout with a low exchangeable-base content at a maximum in the surface horizon, and a high exchange acidity. The C/N ratio of the A_1 horizon is 15; lower values of the ratio in sub-surface horizons confirm the visual impression that there is no downward movement of colloidal humus. Fragments of parent material appear to be undergoing disintegration in the lowest horizon, in which the percentage base saturation is higher than the horizons immediately above. Free sesquioxide

[1] Samples contaminated in transit, so preliminary descriptions not checked in the laboratory.

TABLE 2

Analyses of Samples from Profile No. 8

Horizon (in.)	*0–3″*	*3–13″*	*13–25″*	*25–31″*	*31–48″*	*50–72″*	
Mechanical analysis							
0·5–0·2 mm.	1·7	1·7	3·0	2·9	2·5	5·6	Percentage on air-dry fine earth
Fine sand	55·9	56·9	53·8	45·8	45·1	56·1	
Silt	9·2	10·5	10·2	15·4	11·7	10·9	
Clay	30·4	31·0	33·6	36·5	40·7	27·5	
Organic C	3·5	0·5	0·4	0·3	0·2	0·2	
Nitrogen	0·23	0·06	0·04	0·04	0·04	0·03	
C/N	15·0	9·0	11·0	6·4	6·1	6·1	
Organic matter	5·8	0·9	0·65	0·44	0·43	0·34	
pH in M/100 $CaCl_2$ 1:5	3·54	4·11	4·16	4·20	4·22	4·90	
Free $Fe_2O_3+TiO_2$	1·1	1·2	1·1	1·4	2·4	3·2	Percentage on air-dry fine earth
Free Al_2O_3	..	0·8	0·4	0·4	1·6	1·1	
Free SiO_2	4·1	6·7	3·6	7·1	4·7	4·9	
Exchangeable cations							
'H'	6·39	4·49	4·90	4·92	5·12	3·16	In m.e./100 g. air-dry fine earth
Ca	0·14	0·06	0·09	0·05	0·03	0·03	
Mg	0·44	0·08	0·08	0·04	0·04	0·10	
K	0·02	0·01	0·01	0·01	0·01	0·01	
Na	0·006	0·002	0·006	0·005	0·004	0·009	
% base saturation	8·7%	3·3%	3·7%	2·1%	1·6%	4·6%	
Bulk density	1·32	1·27	1·49	(1·06)	(0·91)	1·48	Air-dry soil
Porosity (air-filled pores)	44%	40%	32%	35%	31%	35%	Soil at field capacity
	25·4%	12%	..	..	..	..	
Total cations (composite sample for whole profile)	K 3·15; Mg 14·65; Ca 7·65 m.e./100 g. air-dry soil						

Note: Mechanical and organic matter analyses by usual methods (assuming a C recovery factor of 75 per cent.); Free silica by digestion in M/2 NaOH at 100° C. for 4 hours; Free sesquioxides by digestion with 5 per cent. sodium hydrosulphite at 50° C. for 20 minutes; Exchangeable cations by NH_4OAc (pH 7) extraction; Exchange acidity by titration of N $CaCl_2$ extract; Total cations by sodium carbonate fusion; Bulk density by Russell and Balcerek (1944) method.

contents also are highest at the base of the profile. Since the silt/clay ratio changes very little up the profile, although silt-sized particles are usually found to be less stable to weathering than clays, it would appear that there may be some downwards translocation of clay to the 31–48 in. horizon.

From the clay mineral analyses mica appears to be weathering through chlorite to vermiculite, and possibly in part to kaolinite.

These profiles are fairly typical of the acid yellow soils found on base-poor parent materials in areas with no dry season and are similar to those described for Brunei (Blackburn and Baker, 1958) and elsewhere in Sarawak (Beckett and Hopkinson, 1961). They should perhaps be grouped with Kellogg's (1949) Red-Yellow Latosols with regard to their profiles and low base content, though they are somewhat more highly leached and yet show less marked horizon differentiation. The Borneo

TABLE 3

Clay Fraction Analyses

	Depth								
Profile No. 3	22–94″	Quartz is apparently the only mineral present.							
	106–8″	A high percentage of quartz and a little kaolin and mica.							
	108″+	Quartz is apparently the only mineral present.							
Profile No. 5	12–20″	A high percentage of quartz and some kaolin.							
	20–23″	95% kaolin, 5% gibbsite, traces vermiculite, anatase, and quartz.							
	23–26″	60% kaolin, 20% mica, 20% chlorite, traces vermiculite, gibbsite, quartz.							
Profile No. 8		*Kaolin*	*Mica*	*Vermiculite*	*Chlorite*	*Boehmite*	*Anatase*	*Goethite*	*Quartz*
	3–13″	35%	15%	40%	10%	..	tr.	tr.	tr.
	31–48″	35%	25%	20%	20%	..	..	tr.	tr.
	50–72″	35%	35%	15%	15%	tr.	..	..	tr.

and Congo soils appear to exemplify stages in the maturity sequence of acid yellow soils. The Bintulu soils apparently represent an earlier stage on a less mature landscape where continuous rejuvenation by creep or surface wash may be more marked than in the Congo profiles. What appear to be later stages in the development of similar profiles are characterized by clay pan horizons with increasingly conspicuous red and white mottles high up the profile, and sometimes by surface accumulations of mor or peaty humus. They have been described for British Honduras (Charter, 1940) and the Amazon basin (Marbut and Manifold, 1926). Stages of the maturity sequence may also be observed in Malaya, where profiles of the Batu Anam (Owen, 1951), Malacca, Padang Gong Chenah, and Kampong Lubok Kiat series (Arnott, 1957) appear to represent soils characteristic of successive stages in the degradation and maturation of a predominantly shale or phyllite landscape, comparable to many areas in Sarawak. On sandy parent materials continued development of the profile may lead to incipient podzolization shown by a mor humus layer and a perceptibly bleached A_2 horizon as in Profile No. 4, under Dipterocarp forest. However, the continuation of this process to form soils similar to those under *kerangas* forest, in which marked A_2 horizons and humus hard-pans are apparent, does not appear to occur on sedentary parent materials at low altitude, except where they are covered by light-textured colluvial or unconsolidated marine deposits, or on sites at the lower end of Yellow Loam catenas. On some upland sites at altitudes above the limit of Pleistocene marine deposition, where temperatures are lower and precipitation is higher, *kerangas* forest is found on flat or gently sloping relief, interdigitating with Dipterocarp forest on steeper sites. Browne (1952) has described the succession of forest types over the sandstone ridge of Gunong Sedang, near Kuching. Peat swamp near the sea is succeeded by gently undulating *kerangas* up to the base of the ridge, where it is interrupted by numerous patches of *empran*. The steep slopes of the hill support a

rich forest of *Dryobalanops* and *Shorea* up to 1,000 ft., reverting sharply to *kerangas* on the comparatively level tops of the main and subsidiary ridges. Richards (1936) has reported similar upland *kerangas* soils, podzolic in character, beneath *kerangas* forest at 3,000 ft. in the Upper Koyan valley by Mt. Dulit. In general it would seem that it is only under conditions of relatively intense leaching at fairly high altitudes that the full succession from yellow loams to podzolic *kerangas* profiles can occur, and then only on sandy parent materials on nearly level sites at which the development of the profile is not curtailed by mass-wasting processes. At lower altitudes and on heavier parent material the succession appears either to be interrupted by creep or deflected towards peat formation.

Soils beneath Kerangas Forest

Kerangas forest[1] has already been described (Richards, 1936; Postumus, 1937; Browne, 1952, 1954). In the Bintulu coastal area it is confined to nearly level terrain. Few trees extend above the upper layer at 90–100 ft. so that the forest can frequently be recognized on aerial photographs by the smoothness of its canopy. Orchids are abundant and also mosses, both low on tree boles and on the ground. There is commonly a thick layer of leaf litter and mor humus. The regeneration of tree species is plentiful and there is no evidence that it is hampered by the accumulation of mor humus.

Tanah kerangas or *kerangas* soil shows a surface accumulation of mor humus and a bleached sandy horizon 12–60 in. deep, often indurated towards the bottom, and resting upon a more or less compact and impermeable humus pan (Plate I.1). Seepage water and streams in areas of *kerangas* soils show a characteristic 'black-water' appearance due to the presence of finely dispersed organic matter. *Kerangas* soils are developed to the greatest extent on areas of level, or nearly level, well-sorted sand, marking former beaches and strand lines, in which nearly free drainage and the absence of relief combine to accelerate the attainment of maturity in the soil profile. On well-developed *kerangas* soils on such sites the feeding roots of the vegetation may be prevented from drawing upon the nutrients in the weathering zone, and in seeping ground water, by the perched water table on the impermeable humus horizon (U.S.D.A., 1927; Jennings, 1957). In this case burning or misuse leading to the destruction of the A_0 or A_1 horizons, and the consequent loss of the only nutrient reserves in the soil,[2] may reduce regeneration and give rise to the open 'Heath Forest' or *padang* vegetation, in

[1] It is characterized by indicator species such as *ru* (*Casuarina sumatrana*), *bindang* (*Agathis dammara* var. *borneensis*), *sempilor* (*Dacrydium becarii* var. *subelatum*), and *kawi* (*Whiteodendron moultanian*). There are several *Nepenthes* spp., with low palm-like plants of the *Licuala* spp., Calamus climbers, and Lycopodium.

[2] Analyses for total cations present in composite samples of the A_0 and A_1 horizons of several *kerangas* soils gave:

A_0: K 0·42; Mg 6·70; Ca 6·80 m.e./100 g.

A_1: K 0·25; Mg 4·15; Ca 4·70 m.e./100 g.

The cation content of the A_2 horizons of beach terrace *kerangas* soils is extremely low.

which scattered groups of small trees over a ground story of thick moss are separated by areas of white sands, bare or covered only by thin patches of lichens (e.g. Poshumus, 1937). The result is broadly comparable to the Zandery savannah of the 'bleached Dek soils' of Surinam (van der Eyk, 1957). It is difficult to avoid the conclusion that the supply of bases derived from sea-spray or spume may play a significant role in the nutrient cycle of some *padang* or *kerangas* soils. Table 4 indicates the notably greater sodium and magnesium content of composite leaf samples from coastal than from inland *kerangas* forest.

TABLE 4

Analyses of Composite Leaf Samples from Kerangas Forest

	Ash	Na	K	Mg	Ca	Na	K	Mg	Ca
	% on air dry leaves					moles % of cations			
Coastal sample .	3·63	0·062	0·19	0·063	0·18	18	33	18	31
Inland sample .	4·03	0·017	0·77	0·116	0·79	2	44	11	44

Kerangas soils are also found, normally in less extreme form, on the older and higher terraces of river or estuarine alluvium, in the latter case often bounded by a seaward ridge of sand.

The following is by no means an extreme example of a coastal *kerangas* soil:

Profile No. 3

Beneath a secondary growth of ferns, lalang grass, and climbers on the brow of a flat-topped hill, possibly the relic of a former beach, ½ mile inland from the coast at about 100 ft. above sea-level and ¼ mile south of the S. Simulajau.

1½–0″ Partly decomposed litter, with much root fibre.

0–7½″ Brown single-grained fine sand (7·5 YR 5/2) with some bleached sand grains and some grains humus coated; numerous small roots; sharp boundary to

7½–22″ Loose light grey (2·5 YR 7/2) uniform fine sand with slight reddish staining round roots; a few dead roots; merging to

22–94″ Loose single-grained white (10 YR 7/1) fine sand, with gritty quartz fragments; no roots; merging to

94–106″ Loose single-grained white (10 YR 7/1) gritty fine sand, with frequent quartz fragments up to 3 mm. diameter, but few greater than 5 mm.; no roots; abrupt boundary to

106–108″ White very fine sand (10 YR 7/1); hard, compact, and structureless; breaking into large blocks; friable when moist; non-sticky, non-plastic; abrupt change to

108″+ Strongly humic dark reddish-brown (5 YR 2/2) indurated fine sand; porous and structureless, breaking into small clods.

Soils with similar profiles continue down a gentle slope as far as the crest of the 30–40 ft. sides of the river valley, where they are succeeded by Yellow Loam profiles, followed at the foot of the slope by mangrove swamp.

Profile No. 5, sited at the lower end of a gentle slope, shows less extreme profile development.

Profile No. 5

Beneath *kerangas* forest on a gentle seaward slope, ¼ mile inland from the coast and 1 mile SW. of S. Likau, 50 ft. above sea-level. This profile is the lowest member of transect A–A.

0–8″	Matted root fibres and loose fine sand; merging into
8–12″	'Grey brown single-grained fine sand with numerous small live, and some dead roots, considerable humus';[1] sharp boundary to
12–20″	Light grey (10 YR 7/1) loose fine sand; a few live roots; sharp boundary to
20–23″	Dark brown (7·5 YR 3/2) fine sand; compact but friable; weakly developed laminar structure; some dead and no living roots; marked increase in humus content; abrupt change to
23–26″	Very pale brown (10 YR 7/4) fine sandy clay loam; porous, structureless; slightly hard, slightly sticky; non-plastic; some dead, no live roots; merging to
26–44″	Very pale brown fine sandy clay loam; structureless; very finely porous; slightly hard, non-sticky, non-plastic; a few roots; merging to
44″+	Very pale brown fine sandy clay loam, single-grained; a few root remains.

Soils with comparable profiles extend towards the crest of the rise, to be succeeded by Yellow Loam profiles on the steeper reverse slope, down to a Recent alluvial terrace in the valley of the S. Likau. A forest enumeration round the site of pit No. 5 gave 470 Hoppus feet/acre of merchantable timber.

Soils of this type are widely distributed throughout the world on the sandy marine deposits usually associated with an emerging shore-line. In Borneo, Richards (1936) reports a similar profile near Marudi on a sandy platform not more than 50 ft. above sea-level, while Hardon (1937) and Postumus (1937) describe similar soils on the sandy terrace of the Loewai Padang in SE. Kalimantan, 80–90 m. above sea-level, and refer to similar profiles in Sumatra, Bangka, Biliton, and the Celebes.

Tables 3 and 5 give the results of analyses, of which the following features confirm the essential similarity of Profile No. 3 to Ground Water Podzols described elsewhere:

1. Surface accumulations of mor or peaty humus and the associated A_1 horizons, with a low pH, high C/N ratio, and relatively high exchange acidity, nevertheless contain most of the nutrient reserves of the profile above the weathering zone.

2. An almost complete absence of bases, silt, or sesquioxides in the A_2 horizons, in which the curiously high pH (5–6·5) is the consequence of the absence of any buffer system. The indurated horizon above the humus pan, characterized by increased 'free and soluble silica' contents is also typical. It may prove to occur only in profiles in which the B horizon has penetrated to the local ground water-table, or to a water-table perched on heavier-textured facies of the underlying rock.

3. The humus pan shows an exceptionally high C/N ratio (40·2 and

[1] This sample was contaminated in transit. The preliminary field description, therefore, could not be checked in the laboratory.

TABLE 5

Analyses of Samples from Profile No. 3

Depth of sample	1½–0″	0–7½″	7½–22″	22–94″	94–106″	106–8″	108″+	
Mechanical analysis								
2–1·5 mm.	..	nil	0·03	1·05	nil	nil	1·65	Percentage on air-dry fine earth
1·5–1 mm.	..	3·28	0·04	0·48	4·47	0·58	0·67	
1–0·5 mm.	..	3·40	8·18	9·42	13·14	1·24	7·32	
0·5–0·2 mm.	..	38·14	57·92	54·52	20·18	12·90	32·01	
Fine sand	..	20·96	20·97	19·60	48·85	49·54	43·18	
Silt	..	0·63	nil	nil	nil	22·59	nil	
Clay	..	16·20	12·84	15·70	13·34	13·45	15·14	
Organic C	..	2·8	0·14	0·05	0·05	0·08	3·1	
Nitrogen	..	0·086	..	..	..	..	0·039	
C/N	..	32·6	..	..	..	..	77·9	
Organic matter	..	4·8	0·25	0·07	0·09	0·13	5·2	
pH in M/100 $CaCl_2$								
1:2	..	..	..	6·54	6·28	5·20	..	
1:5	3·12	3·32	5·82	6·56	6·32	6·00	3·68	
1:10	..	..	..	6·62	6·48	6·05	..	
Free $Fe_2O_3+TiO_2$	..	nil	nil	nil	nil	nil	nil	Percentage on air-dry fine earth
Free Al_2O_3	..	nil	nil	nil	nil	nil	nil	
Free SiO_2	..	3·84	1·44	5·87	2·55	7·91	3·67	
'Soluble SiO_2' (relative values only)	..	16·5	..	9·5	8·5	12·5	4·5	
Exchangeable cations								
'H'	..	1·31	..	0·13	0·07	0·09	3·61	In m.e./ 100 g. air-dry fine earth
Ca	..	0·36	..	..	..	0·20	0·28	
Mg	..	0·37	..	..	..	0·09	0·20	
K	..	0·009	..	..	..	0·003	0·011	
Na	..	0·010	..	..	..	0·003	0·025	
% Base saturation	..	36·5%	..	..	..	..	12·5%	

Note: Analytical methods as for Table 2; 'Soluble silica' is a relative measure only (uncalibrated ammonium molybdate method) of silica in water extract.

77·9 in profiles Nos. 3 and 5), low pH, and a relatively higher cation exchange capacity than the organic matter of the A_1 horizon. A low content of iron (confirmed by ignition) and free sesquioxides is also characteristic, except in those profiles reported elsewhere in which the humus pan is in contact with ferruginous ground water (e.g. Leneuf, 1956) or rests on heavy-textured material with some content of free iron oxides (e.g. Thorp and Smith, 1933; van der Eyk, 1957).

The pan in profile No. 5 appears to owe its position to such a change in texture. Mica and chlorite give place to kaolinite and a little gibbsite (Table 3) between the 23–26 in. and 20–23 in. horizon. The transition may at least in part be the consequence of a high intensity of weathering at the advancing front of the organic horizon, possibly due to the displacement of hydrions during the formation of aluminium complexes (Martin and Reeve, 1957) from illuviated acid humic compounds.

Low-level *kerangas* soils supporting *kerangas* forest commonly occur as the lower members of the Yellow Loam (Dipterocarp) catena. A transect (A–A on Fig. 1) up the slope from profile No. 5 as far as a yellow loam profile on the steeper (15°) reverse slope is shown diagram-

matically in Fig. 2, and on Plates I.2, II.3 and 4. Mass-wasting is more rapid on the slope and may counteract podzolization. In some cases the low-level *kerangas* soils may owe their formation to accumulations of light-textured downwash. In other cases such explanations do not seem

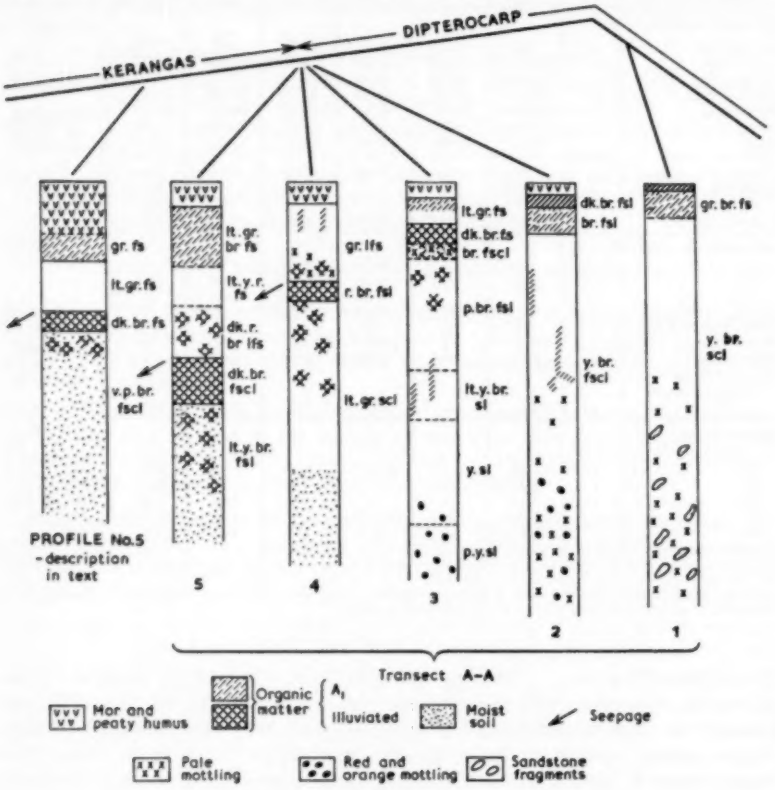


FIG. 2

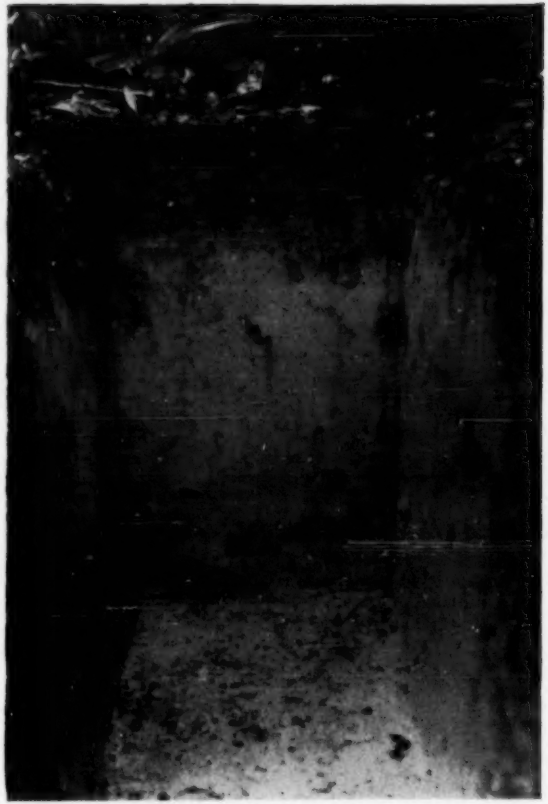
to apply and we can only suppose that the transition from the latosolic to the podzolic succession is due to the greater accumulation of litter, tending to produce peat podzols, in the wet foot-slope position. Whereas the yellow loam profiles were drained rapidly to at least 50 in. after heavy rain the low-level *kerangas* soils showed a perched water-table on the B horizon, and a lower water-table in the parent material at 40–50 in., separated by a zone of relatively dry soil. Most seepage occurred from the perched water-table.

Less commonly, on parent materials heavy enough to possess adequate nutrient status, the lower numbers of the yellow loam catena support *empran* forest and correspond to *tanah bakar*. Fig. 3 indicates the two

1. Deep *kerangas* soil—B horizon exposed to the left of the forest guard.

2. The lower end of the trench on the S. Simulajau transect (B–B) showing the transition from Yellow Loam to low-level *kerangas* profiles.

T. W. W. WOOD AND P. H. T. BECKETT—PLATE I



3. Stage No. 2 on the S. Likau transect (A–A) showing the transition from Yellow Loam to low-level *kerangas* profiles.

4. Stage No. 4 on the S. Likau transect, showing shallow A_0 horizon, thin A_1 horizon, and marked organic B horizon on and in the heavy textured material below the top joint of the ruler.

extreme forms of the catena. All intergrades between the two extreme forms occur and all of them grade into low-level freshwater swamp or mangrove swamp soils.

The low-level *kerangas* soils differ from those on beach terraces mainly in being less highly developed, the A_2 horizon not often exceeding 20–30 in. in thickness, and frequently also in their much more diffuse humus B horizons, indurated only locally or not at all. B-horizons

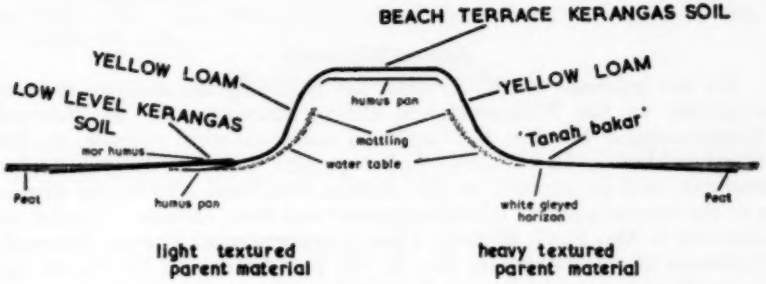


FIG. 3

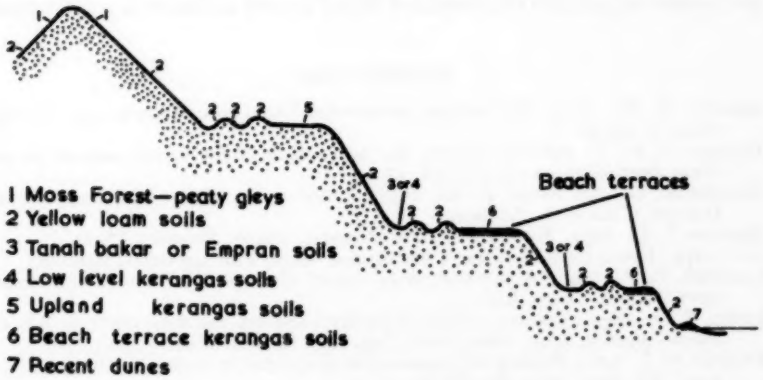

1 Moss Forest—peaty gleys
2 Yellow loam soils
3 Tanah bakar or Empran soils
4 Low level kerangas soils
5 Upland kerangas soils
6 Beach terrace kerangas soils
7 Recent dunes
Beach terraces

FIG. 4

of low-level *kerangas* soils extend downwards some distance into the heavier textured underlying horizons in the form of organic stains on structure faces, alternating with more or less white mottling, which gives place to red and orange mottling above the lower water-table. As the texture of the underlying material becomes heavier the B horizon becomes more diffuse and more highly mottled (Plate II.4). Transect B–B across the junction between the country rock and a former terrace showed how as the lighter material feathered out upslope, the depth to the humus B horizon and its sharpness decreased, until near the *kerangas*–Dipterocarp boundary the soil profile differed from the normal yellow loam

profile only in showing slightly enhanced litter and A_1 horizons (Plate II.3). The single-grained sands of *kerangas* A_2 horizons are very liable to creep or erosion and the lowest member of this transect consisted of a *kerangas* profile superimposed upon layered alluvial/colluvial deposits of clay and humic sand.

In summary Fig. 4 represents what appear to be the most common relationships in the distribution of the dominant Yellow Loam and *kerangas* profiles.

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INVESTIGATIONS ON RICE-GROWING IN BRITISH GUIANA

I. CHARACTERISTICS OF SOME RICE SOILS OF THE COASTLAND

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Summary

An attempt has been made to account for the different soil types which are derived from alluvial material of similar age and origin. The sequence noted was undifferentiated alluvium (frontland clay soil), humose clay (pegassy-clay soil), thin organic soils (pegasse). The subsoil varied from that similar to frontland clay to a bleached yellowish-white structureless clay. Differing durations and intensities of flooding were considered to be responsible for the changes in the subsoil. With permanent flooding, plant residues accumulate on the surface and the soil is more rapidly leached. Less organic matter accumulates and less leaching occurs with seasonal flooding. Reefs of dry sand and other soils develop under special conditions and, as they do not belong to the general sequence, are described separately.

Introduction

THE coastal soils of British Guiana are derived from marine alluvium, carried by the north-west current along the north-east coast of South America from the mouth of the Amazon. The deposition of sediment with further extension of the land seawards is continuing. The coastal sediments, with a proved maximum depth of 6,000 ft., have been divided into three formations based largely on their lithology and order of superposition (Bleackley, 1955). The most recent formation, the Demerara clay, occurs as a strip about 25 miles wide along the entire coast. The average thickness along the coast is 150 ft., decreasing in a south-westerly direction to meet the underlying formation. The soil profiles described below were all within 5 miles of the coast and represent the most recent deposits. The following descriptions refer only to this strip, part of which had been empoldered and was the area most intensively cultivated. No soil maps and few profile descriptions of the various soil types were available. Hardy (1953) has classified the coastal soils as follows:

1. Frontland clay-Solonchak (Intrazonal; halomorphic)

Originally it was probably covered by swamp and marsh vegetation and was saturated with sea-water. The surface layers have been drained since the area was brought under cultivation. The subsoil water has the same composition as diluted sea-water. The topsoil is highly acid but acidity disappears with depth. The surface is brown clay with much ferruginous mottling overlying a stiff grey or blue-grey clay with much ferruginous mottling.

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2. Pegassy-clay and pegasse-Half-bog and bog soils (Intrazonal; hydromorphic)

Originally they were occupied by arboraceous freshwater swamp vegetation. They are typical 'tropical peat' soils. The subsoil is usually a bleached yellowish-white to white structureless clay, but pegassy-clays are known overlying typical frontland clay subsoils and intermediate types. They are highly acid and acidity increases with depth except where the subsoil is saline. The organic matter content may reach 80 per cent.

3. Riverside silt-Alluvial (Azonal)

Originally it comprised levees and marsh forest. Drainage and leaching are converting it into podzolic types. The topsoil is yellow or orange mottled below. The soil is highly acid and acidity increases with depth.

4. Reef sand-Dry sand (Azonal)

It comprises low banks and dunes in patches in the frontlands.

In addition, two special soil types were found which warranted separate classification.

5. Cane Grove soils

The surface layer consisted of black humose clay (pegassy-clay) overlying a grey clay with ferruginous mottling. Below this was a second organic layer followed by a grey clay. The depths of the intermediate clay and organic layers varied from 2–3 in. to 50–60 in.

6. Reef clays

In places along the coast two or more sand reefs were found parallel to the coast and separated from one another by distances of one to two miles. Between the reefs, a lens of clay or silty-clay had been deposited. These soils differed from the frontland clays in having a freely draining subsoil.

Experimental

The profiles examined were from the sites of field experiments scattered throughout the rice-growing areas. All profiles were sampled to the permanent water-table. The soils were examined for their pH, salt content, exchangeable bases (Ca, Mg, K, Na, and Al), organic C, total N, and mechanical analysis.

Analytical methods

pH was measured in a soil to water suspension of 1:2·5. Total salt content was determined conductimetrically in a soil to water suspension of 1:5 (Piper, 1950, p. 36). Exchangeable bases were extracted by leaching with neutral normal ammonium acetate. Calcium and magnesium were determined by the method of Cheng and Bray (1951). Sodium and potassium were both determined photometrically with an 'EEL' flame photometer. Aluminium was determined colorimetrically by the method of Chenery (1948). Organic C was determined by the method of Walkley and Black (Piper, 1950, p. 223). Total N was determined by the Kjeldahl method. Mechanical analysis: 50 g. soil was dispersed by shaking with 500 ml. water and 25 ml. of 5 per cent. sodium hexametaphosphate solution containing 0·75 per cent. sodium carbonate.

The suspension was transferred to a 1,000-ml. graduated cylinder and made to the mark with water. After mixing, the suspension was allowed to settle for the appropriate time before sampling (Piper, 1950, p. 76). The sample was dried to constant weight at 105° C., and this was corrected for the sodium hexametaphosphate. All results are calculated on an air-dry basis.

Results

1. *Frontland clay soil*

One profile was examined in the Rice Experiment Station, Botanic Gardens, Georgetown.

Profile A

0–6 in.	Soft blue-grey clay with moderate amount of ferruginous mottling.
7–36 in.	Stiff blue-grey structureless clay with chocolate-brown mottling and ferruginous and chocolate-brown soft and hard concretions.

Table 1 shows that pH and salt content increased with depth. Exchangeable Ca was uniform down the profile, but exchangeable Mg increased slightly below the cultivated layer. Both exchangeable K and Na increased with depth. Exchangeable Al was uniformly low throughout. Organic C and total N contents were normal for this soil type and decreased with depth. The soil was clay throughout.

2. *Pegassy-clay soils*

Two profiles were examined. Profile B was at the Mahaicony Abary Rice Development Scheme, East Coast, Demerara, and Profile C at Coffee Grove, Essequibo Coast. Both had the characteristic dark humose clay surface layer of this soil type.

Profile B

0–6 in.	Black humose clay.
7–48 in.	Blue-grey clay with much ferruginous mottling.
49–54 in.	Ferruginous fine sandy clay.

Table 2*a* shows pH increased with depth, the soil becoming alkaline below 18 in. From the surface to 48 in. the soil was clay containing about 50 per cent. clay and less than 7 per cent. sand. The 49–54-in. layer contained 43 per cent. clay and 19 per cent. sand. Salt content increased with depth to 48 in., and then decreased in the sandy clay layer. Exchangeable Ca, Mg, and Na increased below the surface layer, with maximum values from 7 to 18 in., and slightly lower ones from 19 to 48 in. In the sandy clay layer at 49–54 in., they had values about the same as the surface. Exchangeable K had its maximum value in the surface layer, its minimum value in the one below, and then increased with depth. Exchangeable Al had accumulated in the surface layer. Organic C was higher than in the frontland clay soil and the C/N ratio of the organic matter was also slightly higher.

Profile C

0–12 in.	Dark grey-black humose clay with little ferruginous mottling.
13–15 in.	Light brown-grey clay with little ferruginous mottling.
16–36 in.	Light grey-blue clay with much ferruginous mottling.
37–42 in.	Blue-grey clay with much ferruginous mottling and some soft concretions.
43–46 in.	Bluish-green-grey sandy clay.
47–48 in.	Blue-grey sandy clay with some ferruginous mottling and soft concretions.

Some Properties of Rice Soils of the Coastland of British Guiana
(All results expressed on air-dry soil)

Depth in.	pH	Salt content p.p.m.	Exchangeable bases m.e./100 g. Ca	Mg	K	Na	Al p.p.m.	Organic C %	Total N %
Table 1. Frontland clay. Profile A									
0–6	5·6	380	4·1	16·7	0·39	1·0	3	0·84	0·12
7–18	8·0	630	4·6	21·3	0·75	1·7	2	0·35	0·08
19–36	8·3	1,580	4·2	20·9	1·01	3·2	3	0·32	0·07
Table 2a. Pegassy-clay. Profile B									
0–6	5·2	200	3·9	12·4	0·59	1·9	10	2·89	0·38
7–18	7·0	570	5·0	19·0	0·33	3·2	6	0·40	0·17
19–48	7·6	970	4·5	16·5	0·41	3·0	3	0·09	0·03
49–54	7·7	670	3·7	9·4	0·44	2·4	3	0·16	0
Table 2b. Profile C									
0–6	4·8	330	2·4	15·2	0·33	1·7	11	2·80	0·21
7–12	4·7	220	2·5	12·9	0·33	0·9	10	1·99	n.d.
13–30	5·4	580	2·4	20·5	0·29	1·9	7	0·34	n.d.
31–42	6·4	940	2·8	24·0	0·36	2·6	6	n.d.	n.d.
43–46	7·0	880	2·1	15·6	0·38	2·3	8	n.d.	n.d.
Table 3. Riverside soil. Profile D									
0–10	5·1	750	4·0	11·7	0·35	1·8	2	1·19	0·10
11–18	5·4	3,470	5·3	15·7	0·66	3·9	1	0·17	0·06
19–36	6·0	2,650	4·4	14·5	0·50	4·1	2	0·14	0·05
Table 4. Cane Grove soil. Profile E									
0–3	4·2	470	1·4	2·9	0·38	1·0	22	6·84	0·73
4–21	2·8	370	2·7	7·1	0·38	0·9	55	1·76	n.d.
22–60	2·3	650	6·8	11·7	0·29	2·1	132	18·9	0·63
Table 5. Reef-clay soil. Profile F									
0–6	4·7	110	2·4	6·7	0·35	0·7	7	1·10	n.d.
7–12	4·6	490	3·1	7·0	0·35	1·6	17	0·60	0·11
25–36	5·6	1,070	9·0	11·6	0·64	3·1	10	0·33	n.d.
37–42	7·4	300	2·8	6·7	0·39	1·6	7	n.d.	n.d.

At this site the characteristic humose clay layer extended to a depth of 12 in.; between this layer and the blue-grey subsoil was a thin layer of light brown-grey clay with little mottling. Table 2*b* shows pH and salt content increased with depth but the pH only attained the neutral point

at the maximum depth sampled. The soil was clay from the surface to 42 in., below this was a sandy clay layer. Exchangeable Ca varied little down the profile, with the minimum value in the sandy clay layer. Exchangeable Mg and Na decreased from the surface to their minimum values in the lower part of the humose clay layer (7–12 in.); then increased again with depth to their maximum values at 31–42 in., with intermediate ones in the sandy clay layer at 43–46 in. Exchangeable K increased slightly with depth. Exchangeable Al had accumulated in the humose clay layer.

3. *Riverside soil*

One profile was sampled at Rose Hall, Canje, 200 yds. from the river Canje about four miles from its mouth.

Profile D

0–10 in.	Dark grey-brown clay with moderate amount of ferruginous mottling.
11–18 in.	Stiff blue-grey clay with moderate amount of ferruginous mottling.
19–24 in.	Stiff blue-grey clay with much ferruginous mottling and some oxide accumulation as amorphous material and as granules. A thin irregular layer of iron oxide deposition ran through the horizon.
25–36 in.	Stiff blue-grey clay with little ferruginous mottling, which disappeared below 30 in. The soil became wetter and more plastic below 34 in.

Table 3 shows pH increased with depth but was acid to the depth sampled. The minimum salt content was found in the surface layer and the maximum in the layer immediately below this. Exchangeable Ca, Mg, and K varied little, with minimum values in the surface horizon, maximum values in the layer below, and intermediate values below this. Exchangeable Na increased below the surface layer. Exchangeable Al was low in value throughout. Organic C content of the surface soil was low with a C/N ratio of 12. The soil was a silty clay throughout, containing from 41 to 48 per cent. clay and 11 per cent. sand in the surface layer with 16–19 per cent. below this.

4. *Cane Grove soil*

One profile was sampled at Pastureland, Cane Grove Land Settlement, East Coast, Demerara.

Profile E

0–3 in.	Black humose clay.
4–21 in.	Brown-grey clay with ferruginous mottling.
22–60 in.	Dark-brown fibrous organic matter.

Table 4 shows the profile was highly acid, pH decreasing with depth. In the surface layer the values for exchangeable Ca and Mg were less than the other soils, but those for exchangeable K and Na were similar. The profile contained much exchangeable Al, which increased with depth. The organic surface and lower layers had C/N ratios of 9:1 and 30:1.

5. *Reef clay soil*

One profile of this soil type was sampled at Clonbrook, East Coast, Demerara.

Profile F

0–6 in.	Reddish-brown clay on the surface, blue-grey with ferruginous mottling underneath.
7–12 in.	Very firm blue-grey clay with ferruginous mottling.
13–18 in.	Light brown-grey clay of soft consistency with much ferruginous mottling and small pockets of ferric oxide and concretions.
19–24 in.	As above but more concretions. The water-table at the time of sampling was at 21 in.
25–30 in.	Light grey-brown clay with much ferruginous mottling.
31–36 in.	Light brown clay becoming more sandy with depth, much ferruginous mottling and small concretions.
37–42 in.	Ferruginous fine sand with green and black streaks, saturated with water.

In this profile the underlying sand occurred at 36 in. Table 5 shows pH increased with depth but did not become alkaline until the sandy layer and, presumably, groundwater level was reached. Exchangeable bases increased in value with depth until the sandy layer, when they decreased sharply. Exchangeable Al had increased values in the 7–12-in. and 25–36-in. layers. The sandy layer at 37–42 in. contained 85 per cent. sand.

Discussion

As the coastal soils of British Guiana were derived from marine alluvium and were tidally flooded in the natural state, the effects of permanent flooding were considered important in profile development. When the level of the deposits had been raised above the low-water mark, two conditions could give rise to permanent flooding, i.e. the presence of depressions, usually small; or impeded run-off caused by the building up of levees by the sea or rivers, when the areas flooded were often extensive. Permanent flooding promotes reducing conditions in the soil, and plant residues accumulate with the formation of an organic or humose clay (silt, or sand) surface layer. For profile development, downward movement of water through the soil is usually necessary, and a mechanism must be postulated for this to happen in these soils, developed between tidal limits, where such movement appeared unlikely. However, considerable grownd water movement was found by Wilkins (Conference Report, 1955) at sites several miles from the coast or nearest tidal river. The suggestion is made that groundwater withdrawn at low tide causes surface water, if present, to percolate through the soil. The land is reflooded as the tide rises, with no corresponding upward pressure at high tide, so that a net downward movement of water is the result. On this hypothesis the effects of leaching on profile development and characteristics would occur to a depth corresponding to the low-water level. The observations made support this idea.

The surface soils showed a hydrologic sequence from the undifferentiated alluvium (frontland clay) through humose clays (pegassy-clays) to thin organic soils (pegasse). The subsoil of the humose clay and of the organic soils varied from that morphologically similar to the frontland clay to a bleached yellowish-white structureless clay. These shallow organic and humose clay soils were considered to be of similar age to the frontland clay soils; the formation of the surface organic matter and bleaching of the subsoil was the result of varying lengths of time of permanent flooding and consequent reducing conditions. The properties of profile A (frontland clay) compared with profiles B and C (pegassy-clays, of which C was the more leached) showed the general sequence expected. The surface layer of the pegassy-clays was more acid than the frontland clay, pH 5·2 and 4·8 compared with pH 5·6; also the acidity extended to a greater depth in the pegassy-clays, 18 in. and 46 in. compared with 6 in. in the frontland clay. The exchangeable Mg:Ca ratio and exchangeable K values changed with leaching. In the frontland clay the Mg:Ca ratio was 4:1, a value also found by Follett-Smith (1933), but in the more leached pegassy-clay the ratio was 8:1. Exchangeable K increased with depth in the frontland clay, but was substantially constant below the surface layer in the pegassy-clays. The Na:K ratio was higher in both pegassy-clays than in the frontland clay. Exchangeable bases will gradually be lost by leaching, but as the groundwater of these soils has the composition of diluted sea-water the Mg and Na contents are maintained more than the Ca and K with consequent widening of the Mg:Ca and Na:K ratios in the soil. The pegassy-clay soils contained more exchangeable Al than the frontland clay soils, with an accumulation in the surface layer. Increased exchangeable Al in the humose surface layer was also found by Simonson[1] in other samples from the coastlands of British Guiana, and was attributed to the presence of Al-accumulating species among the natural flora.

The exchangeable Mg:Ca ratio in the reef clay soil (profile F) was lower than in the frontland clay soil, varying from 3:1 to 1:1, compared with 4:1. The additional Ca was considered to be the result of biological enrichment during soil formation. In the preliminary report of the detailed soil survey of Blocks I and II, Courantyne, British Guiana, Simonson[1] noted that certain sandy soils on the landward side of sand reefs were alkaline to the surface which was associated with the accumulation of shells from a snail with a very selective habitat. The reef soils occurred in an analogous position and horizons containing considerable amounts of shell fragments were found in other profiles of this soil type. The evidence suggested that these soils were deposited after the formation of the sand reefs and therefore differed from the frontland clay soils in having a freely draining subsoil, and a lower exchangeable Mg:Ca ratio.

The Cane Grove soil described (profile E) represented a type occurring not only in the Guianas but in other parts of the world, which type was discussed at the Conference of the Three Guianas and Venezuela (1955).

[1] Private communication.

Comparisons were made between some soils of the Guianas and the 'Cat-clays' of Holland. It has been found that the latter contains large amounts of sulphate and the theory advanced is that this condition is due to sedimentation in brackish water. Similar sulphate soils have been observed at Cane Grove and on the banks of many inland rivers in British Guiana, near to Paramaribo and other sites on the coastal plains of Surinam, and in the Mana area in North Western French Guiana.

The conditions for the origin of such soils in the Guianas were undoubtedly similar to those in Holland, Finland, and Cambodia. These conditions are brackish water and sedimentation accompanied by decaying organic matter under reducing conditions. It is presumed that the soils at Cane Grove were formed under such conditions, and there was speculation as to whether the organic matter was peat or came from the roots of trees. The colour of these horizons whether peaty or not is much darker than normal. Upon drying, yellow streaks and coatings of basic iron sulphate form on the surface of clods but this coloration is not present on the fresh wet material. There are also large pH changes upon air-drying of the soil, with a drop of as much as 6 full pH units reported from Finland. Usually the drop is considerably less.

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PEDOGENESIS OF SOME RED-BROWN EARTHS BASED ON TRACE-ELEMENT PROFILES

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Summary

The clay profile of six red-brown earths of South Australia formed from sedimentary material was not produced by an eluvial-illuvial process. Analytical data for trace elements provide convincing evidence that the present amount of weathering per unit mass of the parent material decreases with increasing depth throughout the B horizons and that at least all but an insignificant part of the clay content of these horizons was formed in its present position. Most of the clay formed from the surface layers of the parent material has been lost. All observations are accounted for in a simple and straightforward manner.

This result casts doubt on the validity of the term 'illuvial horizon' for any similar soil.

Introduction

A CHARACTERISTIC feature of the red-brown earths of Australia (Stephens, 1956) is the usually marked difference in texture of the A and B_1 horizons. A clay content in the B_1 horizon ten times as great as that in the A horizon is not uncommon. It is generally assumed that such a difference in texture in any soil was produced by eluviation of clay from the A horizon and its deposition lower in the solum. Since red-brown earths have good internal drainage, this assumption is plausible for them. It is, however, only an assumption and the actual determination of the mode of formation of their clay profile has remained an interesting pedological problem.

However this problem is attacked, one of the main difficulties is caused by the variableness of soils of any one taxonomic group. If only one sample is examined, it is not easy to decide which of its features are characteristic of the group and which are accidental (that is, produced by localized variations in pedogenic factors). When a result has been obtained for this single sample it still remains to be shown that the conclusions are valid for all soils of the group, or at least for those developed from similar parent material.

This limitation can be partly overcome by the examination of several samples which are sufficiently dissimilar for the conclusions to have some general validity. Such an examination is facilitated if analytical results for all samples are combined in such a way that characteristic features are accentuated and accidental features are either suppressed or made obvious. In other words, it is helpful to be able to produce an average or idealized clay profile, for instance, from a number of clay profiles which are dissimilar in detail but should have the same characteristic features. A minor disadvantage of this approach is that numerical results are not likely to be correct for any actual soil profile; this is an unavoidable defect in the average for any natural entity.

The procedure used in this study for obtaining an average clay, sand, or any other profile from analytical results for closely related soils was developed for use where only a few results were available for each soil. It was first employed in a determination of the characteristic features, if any, of trace element profiles for soils of one taxonomic group, and the results indicated that useful pedogenic information could be obtained from those trace element profiles for which a well-defined average existed. An attempt was therefore made to secure information on the origin of the average clay profile for some red-brown earths, that possessed well-defined trace element profiles, from the results of routine mechanical analyses and spectrographically determined concentrations of copper, gallium, and vanadium.

Analytical and Other Data

The six profiles selected for examination had originally been included in a set of red-brown earths used for a survey of the trace element status of these soils (McKenzie, 1957). They were collected in the Nuriootpa Area of the Barossa Valley, South Australia, and have been described by Northcote, Russell, and Wells (1954). Detailed results of mechanical analyses have been given by Bond (1955) and of spectrographic analyses for trace elements by McKenzie (1956).

The samples were taken from localities where the relief was either flat or gently sloping, and there was no evidence for serious accretion or surface erosion. Both external and internal drainage were described as good for all profiles, and it may be assumed that eluvial processes were unimpeded throughout the year. The sampling sites may, for the purpose of this study, be considered as randomly located in those parts of the surveyed area where red-brown earths occur. The two most widely separated sites were about seven miles (eleven kilometres) apart while the two closest were a little over half a mile (about a kilometre) apart.

The parent material of all samples was Pleistocene to Recent proluvium derived from Pre-Cambrian calcareous rocks.

Even if the wide separation of the sampling sites is ignored, the six samples still cannot be regarded as simple replicates of one profile. The available data show, for example, that the thickness of the solum varied from 28 to 72 in. (71 to 183 cm.), the mean clay content from 38 to 60 per cent., and the mean copper content from 42 to 71 parts per million. Any conclusion based on these soils should be valid for all red-brown earths in the sampled area and probably for all red-brown earths formed from sedimentary parent material.

Corrections for Real and Apparent Densities

Density measurements had not been made on the soils used in this study; values for another typical red-brown earth formed from sedimentary material, the Urrbrae loam, were taken as representative (J. W. Holmes, private communication). The real densities for the A and B horizons of this soil were 2·64 and 2·72, respectively. The average apparent density for the B horizons was 1·56 when wettest and 1·60 when driest, while the value for the A horizon, wet or dry, was 1·61.

Corrections for such differences between the A and B horizons would do no more than give a misleading semblance of high accuracy to numerical results.

Of considerable importance, however, is the steady increase with depth in the apparent density of the B horizon, wet or dry. A consequence is that concentrations per unit volume differ in varying degree from concentrations per unit mass, the values ordinarily used. The profile of, for instance, clay per unit mass of soil differs in shape from that of clay per unit volume of soil (which corresponds to the actual soil in the field) and the difference varies with the moisture content of the soil. Only the two fundamental profiles in this work, those for clay and gallium, were determined in both forms, for a dry soil. It is easy to visualize by means of these two pairs of profiles the results that would be obtained were the other profiles converted to concentration per unit volume of soil.

Results Derived from the Analytical Data

The analytical data for each soil profile and the depths of sampled horizons were transformed into what may be called *common measure* because all profiles are brought to a common basis. Each depth in a profile was expressed in terms of the thickness of the solum; that is, the depth of the lower boundary of the B horizon was the unit of depth for the profile. The depth of an horizon was defined as the depth of the central plane of the horizon.

Each concentration for samples from any one profile was expressed in terms of the corresponding average concentration; that is, the average concentration became the unit of concentration. For example, if the average concentration of clay in a solum was 50 per cent., then a concentration of 82 per cent. of clay became 1·64, and one of 7 per cent. became 0·14 common measure. The average used for this purpose was the weighted mean for the A plus B horizons, each value on which the mean was based being weighted according to the thickness of the corresponding horizon. This unit was used for all concentrations for a profile, including those for samples from BC horizons. (The division of individual values by their mean produces complications in statistical analyses of the transformed values; corrections were made where necessary.)

The clay contents of all samples from each soil profile were transformed to common measure and the results for the six profiles are recorded in Fig. 1, where the concentration of clay per unit mass of soil is plotted against depth. A sample from the transitional BC horizon was available for each of four of the profiles and the results for these samples appear in the inset. The figure shows clearly that these soils possess a characteristic clay profile. Accidental features are also obvious as points well removed from the main body of points, such as the point to the right at the bottom of the diagram.

In order to obtain the profile for concentration of clay per unit volume of soil, the original data were converted to concentrations per unit volume by use of apparent densities for a dry red-brown earth. Weighted means were calculated for these converted values which were

then transformed to common measure. The final results are recorded in Fig. 1A; included in this figure is the apparent density profile used for the conversion of concentrations per unit mass to concentrations per unit volume. It is again obvious that the six soils possess a characteristic clay profile. The main difference between the two clay profiles is below depth 0·5; the plot for clay per unit mass is non-vertical while that for clay per unit volume is practically vertical at the mean clay content.

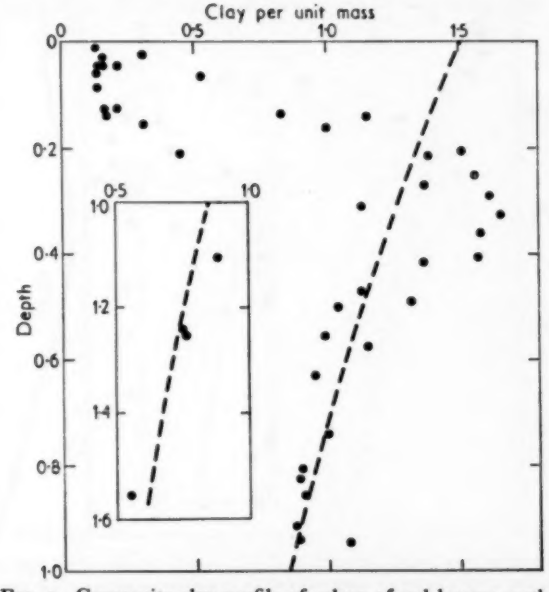

FIG. 1. Composite clay profile of solum of red-brown earths.
Inset: Transitional BC horizon. (Superposed curve fitted to points below depth 0·45 and extrapolated to surface.)

(The density profile for the BC horizon was not known to sufficient depth for conversion of the BC points in Fig. 1.)

The results for the silt-plus-clay fraction, recorded in Fig. 2, show that the soils possess a clearly defined silt-plus-clay profile. Those for the total sand fraction are recorded in Fig. 3 and also delineate a well defined average profile.

Figs. 1, 1A, 2, and 3 show that the six red-brown earths have clearly marked characteristic features and that meaningful averages exist for their clay, silt-plus-clay, and sand profiles. The information supplied by these averages alone could be used to determine processes involved in the development of the clay profile; for example, the shape of the profile in Fig. 1A strongly suggests an eluvial-illuvial process superposed on an originally uniform profile. However, this information is not sufficient for deciding which of the possible processes is the most plausible. The necessary additional information can be obtained from

results derived from the analytical data for gallium, results for copper and vanadium being used as supporting evidence.

The results for gallium are recorded in Figs. 4, 4A, and 5. In Fig. 4 the concentration of gallium per unit mass of soil is plotted against depth, both variables in common measure, and there is a clearly defined

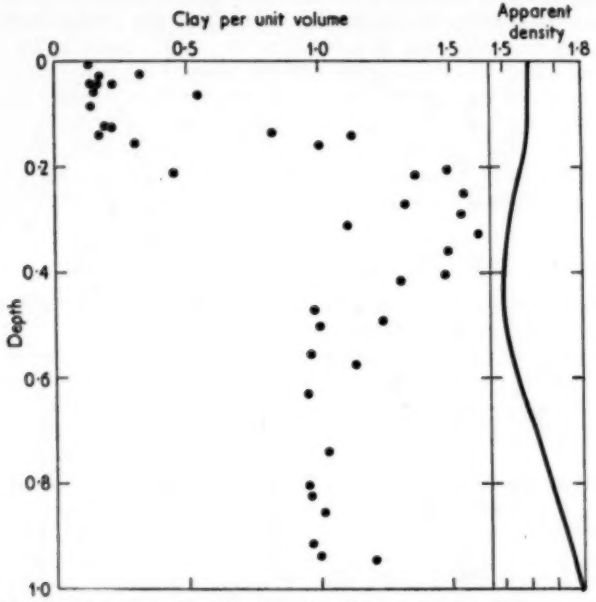

FIG. 1A. Composite clay profile of solum of red-brown earths, with apparent density profile used for conversion of content per unit mass to content per unit volume.

gallium profile below depth 0·2. The profile is ill-defined above this depth, although a statistically significant average can be obtained. Since it is restricted to the surface layers of the solum, however, this poor definition provides useful information. (Fig. 4 may also be taken as a good representation of the corresponding results for vanadium.)

The diagram obtained for the concentration of gallium per unit volume of soil is shown in Fig. 4A. There is again a clearly defined average profile below depth 0·2 and a relative lack of definition above this depth. A comparison of Figs. 4 and 4A shows that the profiles below depth 0·2, as determined by the fitted straight lines, have different slopes (the difference was statistically significant). This difference provides information of great value; in fact, Figs. 4 and 4A contain the solution of the problem under investigation.

Fig. 5 is a plot of the concentration of gallium against that of silt-plus-clay, both concentrations being per unit mass of soil and in common measure. It shows that a close relation exists between these concentrations and can be used to determine the location of gallium in the soils.

An almost identical diagram was obtained for vanadium and a very similar one for copper.

The result obtained by plotting concentration of copper per unit mass of soil against depth is recorded in Fig. 6. There is a clearly defined average profile below depth 0·2, but no average exists above this depth. Thus the results for copper differ from those for gallium because, al-

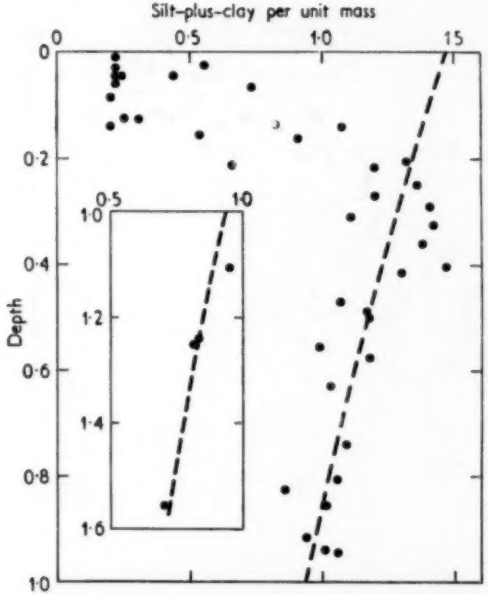

FIG. 2. Composite silt-plus-clay profile of solum of red-brown earths. *Inset*: Transitional BC horizon. (Superposed curve fitted to points below depth 0·2 and extrapolated to surface.)

though it was ill-defined, a significant average profile above depth 0·2 existed for gallium. In other words, the concentration of copper in the surface layers of the soils was more variable than that of gallium.

In order to obtain the results shown in Fig. 7, the concentrations of copper, gallium, and vanadium in any one sample were expressed as fractions of their sum. This figure provides information on the relations between these concentrations and thus on the original composition of the parent material.

Interpretation of the Results for the Trace Elements

As the results for the trace elements are fundamental in the derivation of weathering profiles for the six soils, they must be interpreted first. (The term 'weathering profile' is used here to denote the profile of a product of weathering that remains where it was formed.) This interpretation necessarily involves an assumption about the parent material

because the composition of the relevant part of the material, the part that has become the solum, can only be surmised. As the parent material was a proluvium, a thoroughly mixed sedimentary material, it is probable that there were no systematic changes in composition over depths comparable with those of the soils. If this contention is supported by the results for the trace elements, it may be assumed correct.

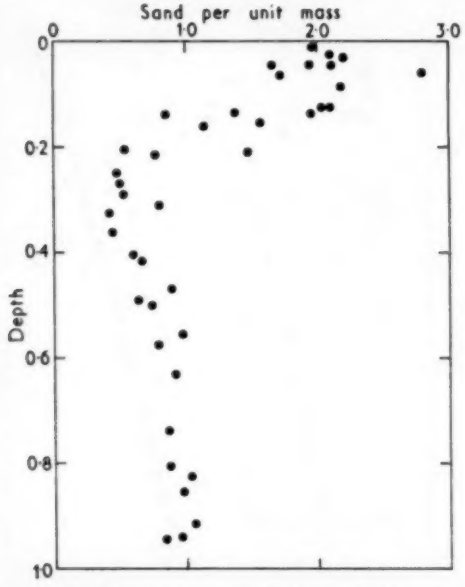

FIG. 3. Composite sand profile of solum of red-brown earths.

Before the results in Fig. 7 are discussed, a few words of explanation are necessary. If the concentrations of, say, copper and gallium are in a constant ratio throughout a solum, then the ratio becomes unity when the concentrations are expressed in common measure, whatever its original value. It follows that, if the concentrations of copper and gallium and of copper and vanadium are in constant, but not necessarily the same, ratios throughout a solum and the concentrations for each horizon are expressed as fractions of their sum, then each value becomes 0·33, common measure being used for all concentrations. Values based on analytical results will, of course, depart from this theoretical value, and the circle in Fig. 7 encloses the area in which most of the points (19 out of each 20) would fall if the departures were attributable to the known analytical errors.

All but one of the 27 points derived from B horizons fall within the circle, and it may therefore be concluded that the concentrations of the three elements were practically constant relative to each other throughout the B horizon of each soil. Most of the points derived from A horizons,

however, fall outside the circle in a systematic manner. The figure shows that this is due mainly to variations in the concentration of copper. When considered alone, the results for the B horizons are no more than compatible with an assumption that the original material had a composition constant with depth at any one site, but they support this assumption when considered together with the results in Figs. 4 and 6.

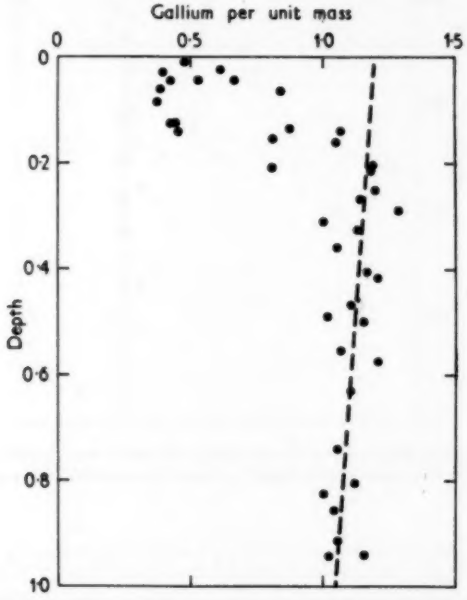

FIG. 4. Composite gallium profile of solum of red-brown earths. (Superposed line fitted to points below depth 0·2 and extrapolated to surface.)

In those two figures the points below depth 0·2, except that just below 0·2 and to the left in each diagram, originated in B horizons. These B horizon points do not depart by more than analytical error from the fitted straight lines; the actual deviations were equivalent to a coefficient of variation of about 6 per cent. for gallium and about 7 per cent. for copper. Both lines have a small but significant slope. Now it is highly improbable that a proluvial material would have had contents of copper and gallium, per unit mass, that varied linearly with depth. The departure from constancy of concentration with depth, in the B horizons, is most plausibly explained as the result of some orderly process acting on an originally uniform material.

Taken together, the results in Figs. 4, 6, and 7 thus strongly suggest that the concentrations of the three trace elements were practically constant with depth at any one site, at least in that part of the parent material from which the present B horizons were formed. Since these elements have markedly different chemical properties, it is reasonable

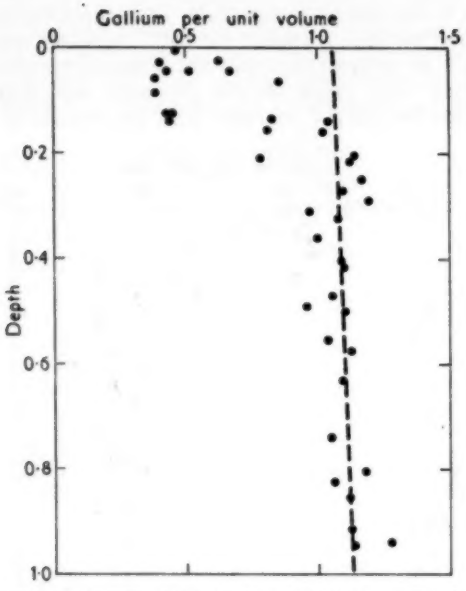

FIG. 4A. Composite gallium profile of solum of red-brown earths. (Superposed line fitted to points below depth 0·2 and extrapolated to surface.)

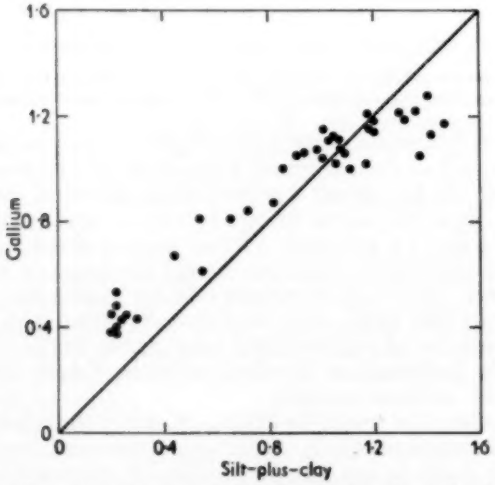

FIG. 5. Relation between gallium and silt-plus-clay in solum of red-brown earths. (Superposed line denotes constant ratio of concentrations.)

to assume that the composition of the original parent material was, on the average, constant with depth at any one site. (The two qualifying phrases—'on the average' and 'at any one site'—are important. It is not assumed that there was no variation with depth at each site; it is assumed only that the haphazard variations at each site were small and would cancel when averaged over a number of sites. It is also not

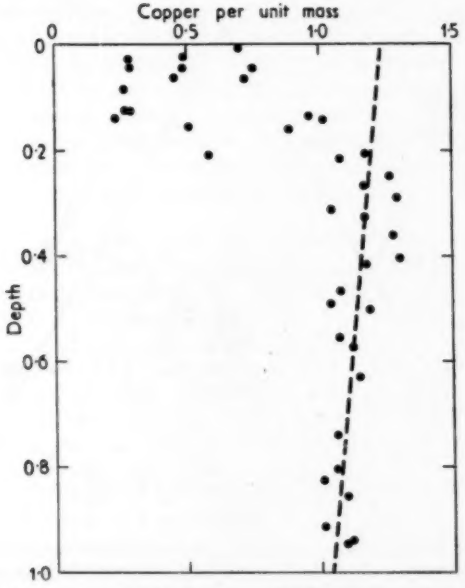

FIG. 6. Composite copper profile of solum of red-brown earths. (Superposed line fitted to points below depth 0·2 and extrapolated to surface.)

assumed that the composition was the same at each site; in fact, the original analytical data indicated that it varied somewhat from site to site.)

The extrapolation of constancy of composition with depth to that part of the parent material from which the present A horizons were derived is, of course, purely assumptive. This layer may have had a very different composition but the only effect on this work would be to make the calculation of losses no more than an artifice for checking the agreement of numerical results and of no factual significance. The main conclusion would be unaltered.

Information on the location of gallium in the soils can be obtained from the results in Fig. 5 on the basis of an assumption about the mode of occurrence of gallium in sedimentary materials. In the light of present chemical and geochemical knowledge about this element (Remy, 1956; Goldschmidt, 1954), the only reasonable assumption is that it occurs as a substitute for aluminium in aluminium-bearing minerals. If all the

gallium in any one soil were present at a constant concentration in the silt-plus-clay fraction, then all the points in Fig. 5 would fall on the line, except for deviations due to analytical errors, whether or not the concentration was the same for each soil (because common measure is used). There is a systematic, and therefore significant, departure at all low concentrations and at the highest concentrations, that is in the A and B_1 horizons of the solum. The apparent excess of gallium in the A

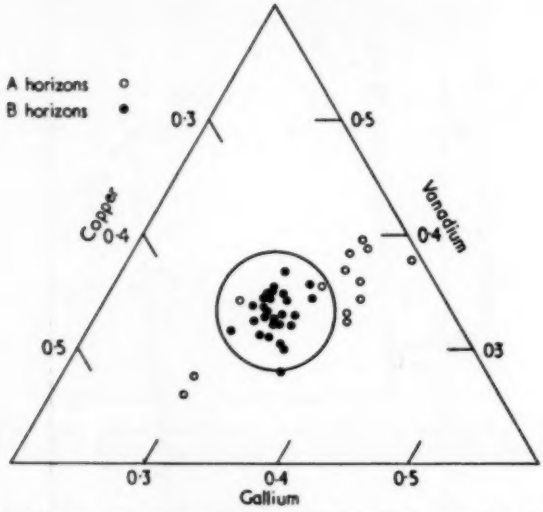

FIG. 7. Relation between copper, gallium, and vanadium in solum of red-brown earths. (Superposed circle encloses deviations attributable to analytical error.)

horizons may be attributed to resistant fragments of aluminosilicate in the predominant sand fraction (Figs. 2 and 3); there has obviously been a concentration of resistant material in the A horizons, whatever the process involved. The apparent deficiency of gallium in the B_1 horizons may, in part, be attributed to the small contribution of the relatively low sand content of these horizons, the remainder of the deficiency being attributable to the presence of significant amounts of non-aluminosilicate clay such as iron oxide. The results in Fig. 5 are therefore consistent with the assumption that all the gallium in the soils was incorporated in aluminosilicates.

The results for vanadium were almost identical with those for gallium (Fig. 5) and it is therefore concluded that the vanadium present in the soils was also incorporated in aluminosilicates. The results for copper showed no apparent excess at low concentrations and a smaller deficiency at the highest concentrations; this can be deduced from Figs. 2, 4, and 6. It is concluded that most of the copper in the soils was incorporated in aluminosilicates, the remainder being partly in organic matter (of which these soils contained very little) and partly adsorbed on the clay.

These conclusions about the mode of occurrence of the trace elements are consistent with the assumption made about the composition of the parent material. It should be observed that they have an important implication: movement of these elements, except movement of a small fraction of the copper, involves movement of aluminosilicates, and conversely.

It still remains to determine the process that resulted in the linear non-vertical profiles of the trace elements below depth 0·2 obtained when concentration per unit mass of soil is plotted against depth (Figs. 4 and 6). One possible process is eluviation of the elements, and therefore of aluminosilicate clay, from the A horizons and their deposition throughout the entire B horizon. Another is transformation of minerals with a lower concentration per unit mass of these elements to minerals with a higher concentration by weathering which decreased in intensity as depth increased. The former is rejected, and the latter accepted, for the following reasons.

Analyses of the sand, silt, and clay fractions of samples from the surface horizon and a median B horizon of two of the soils showed that the concentrations of gallium in the four silt fractions were less than those in the clay fractions, while the concentrations in the sand fractions were lower still (R. M. McKenzie, private communication). Now the concentration of gallium in the average soil at depth 0·2 is about 12 per cent. greater than at depth 1·0 (Fig. 4) and the translocation of a moderate amount of clay would have sufficed to produce this difference because clay with the higher gallium content would have displaced mainly sand with the lower gallium content (the silt content of these soils averaged about 6 per cent.). It must be assumed that the gallium-bearing fraction of the clay was deposited in a systematic manner, per unit mass of soil, throughout the entire B horizon whether the solum was shallow or deep. In addition, it must be assumed that gallium-free, non-aluminosilicate clay was translocated and deposited in the manner required to produce the observed difference in the shapes of the clay and gallium profiles below depth 0·2 (Figs. 1 and 4).

One result of such translocation would be a close relation between the concentrations of gallium and clay per unit mass in the B horizons, a relation that would account for the dependence of gallium content on depth. There was no evidence for even a loose relation between the two concentrations. Not only does the assumption of the translocation of clay entail a complex mechanism but it also lacks factual support.

On the other hand, the observed change in the concentration of gallium per unit mass of soil below depth 0·2 would be the straightforward and expected outcome of the weathering of a uniform parent material if the degree of weathering had decreased steadily with increasing depth and if the concentration of gallium per unit mass had increased as particle size decreased. In this case the amount of gallium originally present in unit mass of the parent material would still be present in the derived soil (unless significant amounts of aluminosilicate had been lost) and the existence of any relation between contents of gallium and certain sized particles would depend on the relative values of the concentrations

of gallium in sand, silt, and clay. It was found that the change in concentration of gallium with depth could be entirely attributed to the relation between contents of gallium and silt-plus-clay. This was in accord with the analyses mentioned above which indicated that most of the gallium content was in the non-sand fraction (as is also shown by Fig. 5).

The increase in concentration of gallium per unit mass with decreasing particle size shows that loss of material occurred as parent material became B horizon. If there was at most only a small change in volume and any loss of gallium was constant within analytical error, then the concentration of gallium per unit volume of soil should be practically constant throughout the B horizons, since it has been assumed that the parent material was uniform. Now the points below depth 0·2 in Fig. 4A, except that on the left which originated in an A horizon, do not depart by more than analytical error from the fitted line and this line does not differ significantly from a vertical line drawn through the mean gallium concentration for the B horizons, 1·10 common measure. This means that the concentration of gallium per unit volume of soil did not show any significant departure from constancy in the entire B horizon. Such a result is incompatible with translocation of clay unless a very complex mechanism for its deposition is also assumed, but it follows automatically from a simple law of weathering provided only that little change in volume occurred as the sedimentary parent material became B horizon.

It is thus clear that a necessary concomitant of an eluvial-illuvial process is a mechanism for translocation and deposition of clay which ensures that the properties of the solum, with respect to the concentrations of gallium, copper, and vanadium, and to apparent density, are indistinguishable from those of a solum produced by weathering alone. Until factual evidence to the contrary is obtained, the only reasonable conclusion is that the red-brown earths under investigation were the product of simple weathering.

If it is assumed that the parent material that has become A horizon had the same composition as the lower layers, then the gallium profiles for this horizon, above depth 0·2 in Figs. 4 and 4A, lead to the conclusion that gallium has been lost. Extrapolation of the linear profile below depth 0·2 in Fig. 4 to the present surface of the solum gives the gallium profile of a soil with an average gallium content of 1·12 common measure. As the actual average is unity, a first estimate of the loss is an amount equal to 12 per cent. of the present gallium content of the solum. This is only a first estimate because loss of gallium entails loss of aluminosilicate clay and loss of clay implies a collapse of the original surface layers of the parent material.

Similarly, the linear profile of Fig. 4A yields a first estimate of the loss of gallium as an amount equal to 10 per cent. of the present content of the solum. This value does not differ significantly from the previous estimate, 12 per cent. As the two values are estimates of the same quantity, they illustrate the precision of such estimates.

Application of the same procedure to Fig. 6 gave an amount equal to 14 per cent. of the present content as the first estimate of the loss

of copper, and the corresponding value for vanadium was 10 per cent. The values for the three elements do not differ significantly, and the average, 12 per cent., is taken as the first estimate of the loss of each element.

The main results derived from the trace-element profiles may be summarized as follows. Below depth 0·2 (common measure) weathering of aluminosilicates has occurred to a degree that varies with depth according to some simple law. Above this depth the prolonged action of pedogenic factors has caused solution of clay which has been leached from the solum in the same way, presumably, as other lost material. Since the greater part, but not all, of the total content of the three trace elements is contained in the dominant clay fraction of these soils (the mean content of clay was 50 per cent. and that of silt was 6 per cent.), a first estimate of the loss of aluminosilicate clay is an amount somewhat greater than 12 per cent. of the present content of the solum.

If an estimate of loss based on the clay profile is compatible with those based on trace element profiles, then the conclusion that weathering alone produced the B horizon receives additional support. This is so whether or not loss actually occurred because each estimate is based solely on the form and location of a curve below depth 0·2. The estimated loss has factual significance only if the extrapolation of uniformity of parent material to the surface layers was correct.

Determination of Weathering Profiles

The results for gallium were examined when expressed as concentrations per unit mass and also as concentrations per unit volume, but work on the results of mechanical analyses was done only with concentrations per unit mass. This was partly because these were the values actually determined and therefore the more reliable, but mainly because it seemed that they were the correct values for use in the determination of a law of weathering.

The array of points below depth 0·2 in Fig. 1 shows that the average clay profile is curvilinear, and a simple exponential form for the equation of a weathering profile for a sedimentary parent material is plausible on theoretical grounds. When such a curve was fitted to the points below depth 0·2, except the point to the left just below depth 0·2 which originated in an A horizon, the fit was unsatisfactory because the points deviated from the curve in a systematic manner.

A satisfactory result was obtained by using only those points from B horizons where the average profile was clearly defined, that is the points below depth 0·45. The fitted exponential curve was extrapolated to depths below 1 where four points from BC horizons were available. The depths of these horizons, the actual clay contents, and the contents predicted by the curve were, in common measure: 1·11—0·89, 0·83; 1·24—0·75, 0·78; 1·25—0·76, 0·78; and 1·55—0·55, 0·67. This excellent agreement indicated that the curve was a good approximation to an actual weathering curve, and its equation was redetermined with the inclusion of the four BC horizon points. The result was

$$\text{clay} = 1{\cdot}51 \exp.(-0{\cdot}57 \times \text{depth}),$$

where clay and depth are in common measure and the expression in brackets is the power to which the number e is raised. The curve is that shown in Fig. 1.

The average deviation of observed values for the clay content from values predicted by the curve, below depth 0·45, was 9 per cent. when expressed as a coefficient of variation. Any evaluation of the significance of this result was precluded by lack of information on the accuracy (not precision) of routine determinations of clay. However, since six soils were used to obtain the points, the deviations are probably not greater than can be attributed to sampling variations and analytical error.

As this weathering curve was based on total contents of clay below depth 0·45, it is a composite curve although the component for alumino-silicates is almost certainly predominant. If it is a good approximation to the general law of weathering for these soils, then a similar curve should be obtained from values for silt-plus-clay.

An exponential curve was fitted to the points below depth 0·2 in Fig. 2, the point to the left being excluded because it originated in an A horizon, and the fit was satisfactory. The curve was extrapolated to the BC horizons, where four points were available, and the fit was so good that the inclusion of these points produced negligible changes in the equation. The result was

$$\text{silt-plus-clay} = 1{\cdot}47 \exp.(-0{\cdot}46 \times \text{depth});$$

the curve appears in Fig. 2.

The average deviation of observed values for the content of silt-plus-clay below depth 0·2 from values predicted by the curve was 9 per cent. when expressed as a coefficient of variation. The comments made on the corresponding value for the curve of Fig. 1 are also applicable here, and the fit is probably as good as could be expected.

Figs. 1 and 2 show clearly that the clay and silt-plus-clay curves differ but little, and a test of the difference showed that it was not significant. This suggests that the curve is an approximate representation of the manner in which intensity of weathering decreases as depth increases, at least below depth 0·2. It should therefore represent the manner in which the content per unit mass of a retained product of weathering decreases as depth increases, provided that the resistance to weathering of remanent parent material is fairly constant.

Extrapolation of the weathering curve of Fig. 1, fitted to points below depth 0·45, up to depth 0·2 is justified by the trace element profiles of Figs. 4, 4A, and 6, and by the silt-plus-clay and sand profiles, Figs. 2 and 3. If it is continued to the present surface of the solum, depth 0, the clay profile so obtained is that of a solum with an average clay content equal to 1·15 common measure. It would appear that the first estimate of the loss of clay is therefore an amount equal to 15 per cent. of the present content, but this is an underestimate.

The area outlined by the points to the right of the upper part of the curve in Fig. 1 indicates a change in the origin or production of clay. Its location and shape suggest translocated clay, but this interpretation cannot be reconciled with the silt-plus-clay, the sand, or the gallium

profiles (Figs. 2, 3, 4, and 4A) all of which show no change in this part of the solum. Therefore the area probably represents clay formed in position; additional evidence for this conclusion is given below. It is thus necessary to account for the lack of accuracy of the law of weathering in this part of the profile.

The actual departure of the average of the observed values in the area under discussion from the value predicted by the curve is small and indicates only a small departure from the law of weathering which was based on the formation of predominantly aluminosilicate clay. Now part of the apparent deficiency of gallium in silt-plus-clay where the values are highest (Fig. 5) was attributed to the presence of significant amounts of non-aluminosilicate clay; evidence for the presence of iron oxide clay, for example, is provided by the red colour of the B_1 horizons. The law of weathering is unlikely to be valid for the formation of non-aluminosilicate clay and the lack of accuracy in the B_1 horizons may therefore be attributed to the presence of a larger portion of this clay than exists in the lower horizons. (The absence of a corresponding failure in the silt-plus-clay curve (Fig. 2) suggests that the composition of silt-plus-clay is fairly constant throughout the B horizons.)

The amount of clay represented by the area was estimated by two independent methods and found to be roughly 5 per cent. of the total clay content of the solum. This clay was not included when the content of the hypothetical solum was estimated because the area is not under the curve. The correct first estimate of the loss of clay is therefore an amount equal to 20 per cent. of the present content of the solum. (The previous estimate would be correct if the clay in question were translocated clay.) Since the mean clay content of the soils was 50 per cent., the estimated loss is equivalent to 10 per cent. of the mineral matter of the solum.

Extrapolation of the curve for silt-plus-clay (Fig. 2) to depth 0 yields 18 per cent. of the present content as the first estimate of the loss of silt-plus-clay. The present mean content was 56 per cent. and therefore the estimated loss is again equivalent to 10 per cent. of the mineral content of the solum. The agreement of the two estimates supports the contention that the area just discussed does not represent translocated clay.

Since the first estimate of the loss of gallium was an amount equal to 12 per cent. of the present content of the solum, it is obvious that the first estimates for gallium and clay agree satisfactorily if the lost clay had roughly the same average composition as the solum. A more precise calculation showed that numerically better agreement was obtained if the lost clay had the average composition of the clay now present in the solum. This agreement provides convincing evidence for the conclusion that the clay profile of these red-brown earths was produced by weathering alone.

Two minor points warrant mention. It may be that the actual concentrations per unit mass of soil for gallium and clay at depth about 0·2 are the maxima under weathering conditions that produce red-brown earths from this parent material. Such an assumption results in no signi-

ficant alterations in the first estimates of loss. The second point is that this work does not show that absolutely no translocation of clay occurred. A small amount would not be detected by the methods employed.

Conclusions

It can be concluded with some confidence that eluviation of clay from the A horizons and its deposition in the B horizons played at most a negligible part in the formation of the clay profile of the six red-brown earths used in this study. Data for trace elements indicate clearly that the present degree of weathering of aluminosilicates decreases in an orderly manner as depth increases throughout the B horizons.

A weathering profile derived from clay and silt-plus-clay contents is consistent with the trace-element profiles and shows that the present clay content of the B horizons was produced in position by weathering alone. There may be a small amount of translocated clay, an amount within the error of the methods used. Most of the clay formed from the surface layers of the parent material has been lost.

The postulated mechanism for the formation of the clay profile accounts for all observations in a consistent and straightforward manner.

Doubt is cast on the validity of the term 'illuvial horizon' for any similar soil.

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CHEMICAL STUDIES OF SOIL ORGANIC MATTER

I. EXTRACTION WITH AQUEOUS SOLUTIONS

JOSEPH TINSLEY[1] AND ABDUS SALAM[2]

Summary

Experiments with an untreated calcareous meadow soil containing 18 per cent. organic matter, and with the sodium soil prepared after treatment with dilute hydrochloric acid, have confirmed that sodium pyrophosphate, citrate, and oxalate solutions are good reagents for partial extraction of organic matter from soils, and have further demonstrated that sodium-sulphite solution is as effective as pyrophosphate at comparable concentrations and pH values. Boiling for 1 hour with 0·5 N sodium pyrophosphate and sulphite solutions at pH 8·4 dissolved almost 40 per cent. of the organic nitrogen from the untreated soil, which is more than double the quantity dissolved by shaking for 24 hours at 18° C.

Introduction

THE extraction of organic matter from soils with aqueous solutions of strong and weak alkalies and with metal complexing salts has recently been reviewed by Tinsley and Salam (1961). It is evident that most workers with aqueous solvents choose either the time-honoured dilute sodium hydroxide or, if a milder reagent is required, sodium pyrophosphate solutions at pH values ranging from 7 to 9.

The purpose of the investigation reported in this paper was to examine a wide range of inorganic and organic salts of sodium and potassium with respect to their solvent powers for soil organic matter compared with 0·5 N sodium hydroxide by prolonged shaking and repeated extraction at room temperature and by boiling.

Experimental

Soil. In these preliminary studies only one soil was used. This was a highly organic calcareous meadow soil taken from the Broad series on the river meadows of the Reading University Farm, Sonning. Full details of the profile have been given by Kay (1936), but the sample was collected only to a depth of 5 in. including the turf, since this surface horizon had a very well-developed granular crumb structure. After drying slowly in air the large sample was ground to pass a 1-mm. sieve, the fragments of grass and roots being picked out by hand as far as possible. The air-dry soil contained 1·11 per cent. of nitrogen corresponding with about 18 per cent. of organic matter. The mineral matter included 8·9 per cent. calcium carbonate and approximately 45 per cent. clay.

Preparation of base-free and sodium-saturated soil

Besides using the soil in its natural calcareous condition, a 2-kg. portion was extracted with 0·5 N hydrochloric acid until free of soluble calcium

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and was then washed with water, filtered, dried gently under infra-red lamps, and reground to pass a 40-mesh sieve. 1 kg. of this base-free soil was then suspended in water and stirred continuously while a 2 N sodium hydroxide solution was dropped in slowly from a burette until the pH of the soil paste reached 7·3. This was dried under infra-red lamps and ground to pass the 40-mesh sieve. The final pH of the soil when shaken with water was 7·08.

Extraction of soils

(i) *Preparation of solutions.* Solutions of 0·2 and 0·5 N sodium and potassium hydroxides and carbonates were used. Inorganic salt solutions were prepared from stock B.D.H. chemicals but the organic salt solutions were mostly prepared and adjusted to pH 7·5 or to 8·3 by neutralizing the required quantity of alkali solution with the appropriate quantity of organic acid.

(ii) *Cold extraction.* Usually 10-g. or 20-g. samples of soil were shaken in stoppered bottles with 100 ml., 200 ml., or other volume, of solution at a room temperature of 18° C. for 24 hours on a Griffin and Tatlock reciprocating shaker.

(iii) *Hot extraction.* Usually 10-g. or 20-g. samples were boiled for 1 hour with the appropriate volume of solution in 500 ml. Pyrex conical flasks fitted with cold-finger condensers as described by Tinsley (1950).

The extracts, cooled when necessary, were centrifuged in 200-ml. bottles at 2,000 g. for 2 hours and the clear supernatant liquid poured off.

Determination of nitrogen

It was decided to use the nitrogen contents of the extracts as an index of extraction, as was done by Bremner and Lees (1949) instead of the carbon contents as was used by Evans (1959) in order to avoid the difficulty of determining soil organic carbon in the extracts prepared with organic salt solutions.

Methods of analysis of soils and extracts

(i) *Determination of calcium carbonate.* Collins's calcimeter.

(ii) *Determination of pH.* Standard glass and calomel—saturated KCl electrodes in conjunction with Marconi pH meter. Measurements in the region of pH 10 are not therefore very accurate.

(iii) *Determination of total nitrogen.* Semi-micro scale.

(*a*) *Soils.* Sufficient finely ground soil to contain about 10 mg. of nitrogen, usually about 1 g., was mixed in a 100-ml. kjeldahl with 1 g. of a catalyst mixture containing 100 parts potassium sulphate, 5 parts powdered hydrated copper sulphate, and 2 parts powdered selenium and wetted with 2 ml. distilled water before digesting with 7 ml. concentrated sulphuric acid for 2 hours. After cooling the digest was diluted to 100 ml. and a suitable aliquot taken for distillation of the ammonia in a Hoskins-type apparatus (1944) into boric acid solution and titration with 0·01 N hydrochloric acid. Normally 10 ml. of a 4 per cent. solution of boric acid was used containing the bromo cresol green–methyl red

indicator mixture recommended by Sobel, Rockenmacher, and Kramer (1944).

(*b*) *Extracts.* A suitable aliquot portion usually 2 ml. or 5 ml. was digested with 1 g. of catalyst mixture and 6 ml. of sulphuric acid, in duplicate, and the ammonia distilled from the whole of the digest.

Experiment 1. Extraction of nitrogen from base-free soil with cold and boiling 0·5 N solutions of sodium and potassium hydroxides, carbonates, and various organic acid salts

The base-free soil contained 1·14 per cent. nitrogen and Table 1 shows the percentage of this dissolved in each extract together with its pH.

TABLE 1

Extraction of Nitrogen from Base-free Soil with Cold and Boiling 0·5 N Sodium and Potassium Salt Solutions

Extraction	*Nitrogen extracted as percentage of total soil N*			
	Cold		*Boiling*	
0·5 N solution	*Sodium*	*Potassium*	*Sodium*	*Potassium*
Hydroxide . . .	41·9	33·1	75·6	68·7
Carbonate . . .	14·2	11·8	61·1	54·5
Oxalate . . .	10·3 (7·5•)	9·0 (7·5•)	28·7 (7·4•)	31·2 (7·4•)
Citrate	10·7 (6·6)	8·3 (6·7)	28·0 (6·7)	29·0 (6·9)
Tartrate . . .	8·2 (5·5)	6·1 (5·8)	18·8 (5·5)	18·2 (5·7)
Lactate. . . .	5·8 (5·4)	4·2 (5·7)	14·0 (5·1)	13·2 (5·5)
Acetate. . . .	2·0 (6·0)	1·7 (6·2)	10·6 (5·9)	9·8 (6·1)
Formate . . .	1·8 (5·2)	1·4 (5·4)	8·2 (5·1)	7·7 (5·3)

• pH values.

For each treatment the hydroxide dissolved most nitrogen, and the carbonate dissolved rather more than the best of the salts. The potassium solutions dissolved slightly less than the corresponding sodium salts except in the case of boiling oxalate and citrate. The final pH of the salt extracts varied greatly, from about 5·2 for formates to 7·4 for the oxalates, and these differences in pH tend to overshadow any specific effects of the anions on the solution of nitrogen. Nevertheless, it is clear that oxalate and citrate are the most effective anions and acetate and formate least so. Boiling for 1 hour dissolved several times more nitrogen than prolonged shaking at room temperature.

Experiment 2. Extraction of nitrogen from sodium soil

Because of the wide variation in pH of the salt extracts from the base-free soil another, extended, series of extractions was made on the sodium soil using solutions of both organic and inorganic salts 0·2 N with respect to sodium. Initially these were all adjusted to pH 8·3. The exchangeable sodium of the soil amounted to 70 m.e. per 100 g. which increased the total sodium of the system to 0·27 N. Hydrosulphite was included in the inorganic anion group because of its reducing properties and because Besser, Montonna, and Smith (1950) found that alkaline sodium

hydro-sulphite solution effectively dissolved lignin from straw when heated under pressure.

The soil contained 1·17 per cent. nitrogen and Table 2 shows the percentage of this amount dissolved by the various solutions under the same conditions as were used for Experiment 1.

Citrate proved the most effective of the organic anions followed by oxalate and tartrate while pyrophosphate proved the best inorganic salt,

TABLE 2

Extraction of Nitrogen from Sodium Soil with Cold and Boiling 0·2 N Sodium Salt Solutions

Salts	Cold pH	Percentage extraction		Boiling pH
		%	%	
Acetate	6·7	9	26	6·4
Succinate	7·0	10	29	6·6
Malonate	7·4	18	39	6·7
Oxalate	7·8	26	43	7·6
Lactate	6·9	16	27	6·3
Malate	7·4	22	38	6·7
Tartrate	7·0	25	40	6·6
Citrate	8·0	29	53	7·5
Phthalate	7·0	10	30	6·5
Water	7·1	29	51	6·6
Hydroxide	..	54	83	..
Carbonate	10·1	28	69	10·2
Bicarbonate	8·5	16	65	9·7
Pyrophosphate	8·6	38	62	8·4
Fluoride	7·8	16	46	8·5
Hydrosulphite	7·4	17	40	7·5
Alk. Hydrosulphite	11·2	43	61	10·0
Sulphate	7·2	10	26	7·4

but the most surprising feature of the results was the high extraction with water alone, about equal to that secured with citrate in both cold and hot treatments. As in Experiment 1, in every case far more organic matter was extracted by boiling than by shaking at 18° C., the average extraction for the eighteen solvents being 51·6 per cent. by boiling compared with 23·1 per cent. by shaking.

Experiment 3. Extraction of nitrogen with salts of reducing sulphur acids at various pH values

It was noted that the silica residues from the kjeldahl digestion of the hydrosulphite extracts were appreciably less than those from other solutions, notably pyrophosphate, and qualitative tests indicated that iron and aluminium were also low. Accordingly a series of extractions was made to examine the suitability of various sulphur compounds with reducing properties. Sodium sulphite, sodium sulphide, and sodium

hydrosulphite were compared with sodium formaldehyde sulphoxylate. According to Bassett and Durrant (1927) this last salt hydrolyses to sulphite and sulphide in solution and heavy metals are precipitated by the sulphide. Because of the large effect of pH on the extraction of organic matter, 10-g. portions of the hydrogen soil were treated with 100 ml. water, 0·05 N, 0·10 N, and 0·20 N sodium hydroxide in which were dissolved the appropriate quantities of each salt equivalent in

TABLE 3

Extraction of Nitrogen with Boiling 0·1 N Salt Solutions of Reducing Sulphur Acids at Various pH Values

Salts	*Added* NaOH	*pH*	*Percentage of* N *extracted*
$Na_2SO_2{\cdot}HCHO$ Sulphoxylate	0	5·2	14·6
	0·05 N	6·8	29·6
	0·10 N	9·4	64·3
	0·20 N	11·2	75·1
$Na_2S_2O_4$ Hydrosulphite	0·05 N	5·4 (6·6)	22·3 (28·9)
	0·10 N	6·7 (9·4)	37·5 (63·2)
	0·20 N	10·3 (10·3)	68·7 (76·2)
Na_2SO_3 Sulphite	0·05 N	6·8 (8·7)	46·4 (60·8)
	0·10 N	9·2 (9·9)	60·2 (74·0)
	0·20 N	11·5 (11·5)	82·9 (90·5)
Na_2S Sulphide	0·05 N	9·9 (9·7)	64·5 (59·1)
	0·10 N	10·9 (10·7)	80·8 (71·2)
	0·20 N	11·4 (11·4)	81·8 (81·4)

Figures in parenthesis with 0·76 ml. 40 per cent. formalin solution added.

sodium to an extra 0·1 N. Because of the presence of formaldehyde in the sulphoxylate a parallel series of extractions was made with an equivalent quantity of formalin added to the other three salts to examine whether the formalin might influence extraction possibly by reaction with any free amino groups. The results given in Table 3 indicate that formalin exerts no appreciable effect on the extraction of nitrogen if allowance is made for the increase in pH that it gives in the hydrosulphite and sulphite solutions presumably by forming addition compounds with the anion. The quantity of nitrogen dissolved appears to depend more on the pH of the solution than on the individual salt. Since sodium sulphite is the most stable of this range of compounds and gave high extraction it was decided to compare it with sodium hydroxide, carbonate, oxalate, pyroborate, pyrophosphate, and sulphate for the direct extraction of the untreated calcareous soil.

Experiment 4. Extraction of nitrogen from untreated calcareous soil with boiling salt solutions

Calcium sulphite, $CaSO_3.2H_2O$, is soluble to the extent of only 0·0043 g. per 100 ml. at 18° C. and 0·0011 g. per 100 ml. at 100° C. com-

pared with 0·24 g. of hydrated calcium sulphate and 0·0007 g. of calcium oxalate, both at about room temperature, so that most of the calcium in the soil should remain in the residue when extracted with sodium sulphite solution. Extractions were carried out by boiling for 1 hour under reflux with the following solutions in the ratio of 10 g. soil to 100 ml. 0·2 N sodium hydroxide, carbonate, pyroborate, oxalate, and sulphate: 0·1, 0·2, and 0·4 N (Na) sodium pyrophosphate; 0·1 and 0·2 N sodium sulphite.

The soil contained 0·972 per cent. of nitrogen and the proportions of this dissolved in each extract are shown in Table 4 together with the pH

TABLE 4

Extraction of Nitrogen from Untreated Meadow Soil with Boiling Alkali and Salt Solutions

	Hydroxide	*Carbonate*	*Oxalate*	*Tetraborate*	*Pyrophosphate*			*Sulphite*		*Sulphate*
	0·2 N	*0·2 N*	*0·2 N*	*0·2 N*	*0·1 N*	*0·2 N*	*0·4 N*	*0·1 N*	*0·2 N*	*0·2 N*
Percentage N extracted	67·0	56·6	47·1	26·0	45·4	49·0	50·7	30·9	40·6	15·0
pH	11·6	10·0	9·8	9·1	8·3	9·1	9·3	8·1	8·5	8·1

values of the extracts. The 0·2 N sulphite solution dissolved 40·6 per cent. of the nitrogen which is considerably more than that extracted by sulphate but less than that dissolved by oxalate and pyrophosphate solutions of the same strength. However, the pH of the sulphite extract was only 8·1 compared with 9·8 and 9·1 for the corresponding oxalate and pyrophosphate solutions. As the concentration of the pyrophosphate was increased from 0·1 to 0·4 N with respect to sodium, the nitrogen in the extract increased from 45·4 to 50·7 per cent. and the pH from 8·3 to 9·3. Bremner and Lees found maximum extraction in the cold with 0·4 N (= 0·1 M) pyrophosphate solution initially adjusted to pH 7.

Experiment 5. Effect of previous washing treatments on cold and boiling extraction with sodium pyroborate, pyrophosphate, and sulphite

Since extracts of the untreated soil contain small amounts of simple nitrogen compounds, principally ammonium and nitrate, besides the organic compounds, an attempt was made to remove the former by shaking the soil with water and with solutions of sodium and potassium chlorides in the ratio of 1 g. per 10 ml. for 24 hours before extracting with salts capable of dispersing the organic matter.

The results in Table 5 show that the main part of the soluble nitrogen was extracted by water and was presumably mostly nitrate. The stronger 0·5 N potassium chloride solution gave the highest extraction of 1·3 per cent. of the total. Cold extraction with 0·5 N pyrophosphate dissolved about 15 per cent. of the total nitrogen and showed little effect of the preliminary washing. Sulphite dissolved less but the difference was

probably due mainly to the lower pH of the sulphite extract, and pyroborate least. The same order was obtained with boiling extraction, but the quantities dissolved were much higher amounting to about one-third of the total with borax, and one-half with pyrophosphate. The preliminary treatments to dissolve simple nitrogen compounds had no significant effect on the amounts dissolved by boiling, and there was little difference between the 0·2 and 0·5 N solutions of pyrophosphate and sulphite.

It was noticed that the extract obtained by boiling with 0·2 N pyrophosphate tended to be gelatinous and did not give a clear solution even

TABLE 5

Extraction of Simple Nitrogen Compounds and Organic Nitrogen Separately

Previous treatment	*Nil*	*Water*	*Sodium chloride*		*Potassium chloride*	
			0·2 N	*0·5 N*	*0·2 N*	*0·5 N*
Percentage of total nitrogen	..	0·97	1·02	1·06	1·09	1·29
Cold extraction						
Pyroborate 0·2 N	5·2	..	6·31	..	..	..
Pyrophosphate 0·5 N	15·4	17·3	..	15·4	..	14·8
Sulphite 0·5 N	7·3	11·6	..	10·1	..	9·6
Boiling extraction						
Pyroborate 0·2 N	33·4	30·6	33·4	..	35·0	..
Pyrophosphate 0·2 N	..	54·9	54·7	..	48·5	..
,, 0·5 N	52·0	50·9	..	50·2	..	51·0
Sulphite 0·2 N	..	36·0	37·0	..	37·5	..
,, 0·5 N	39·5	39·7	..	40·1	..	39·7

after prolonged centrifuging so that the stronger solution is desirable for preparing extracts free of suspended material. The fact that boiling with sulphite or pyrophosphate solutions extracted about three times as much organic nitrogen as cold extraction does not agree with the experience of Bremner and Lees who found little increase on raising the temperature of extraction with neutral pyrophosphate from 22° to 98° C.

Experiment 6. Repeated extraction with cold and boiling solutions of sodium pyroborate, pyrophosphate, and sulphite

Since one cold extraction dissolves so little it was thought that re-extraction of the soil residue might dissolve quantities of organic nitrogen approaching more nearly those removed by boiling. A series of extractions were made as in the previous experiment but the soil residue was re-extracted twice with fresh solution. 0·5 N solutions of sodium sulphite and pyrophosphate were compared with 0·2 N pyroborate since a saturated solution of the latter is less than 0·25 N.

In calculating the results shown in Table 6, allowance was made for the quantities of the first and second extracts retained in the soil residue when fresh solution was added. Clearly, less nitrogen is extracted each

time both hot and cold and it is a puzzle to understand why so much of the organic nitrogen is retained by the soil. The volumes of solution retained by the soil residue show how pyrophosphate causes most swelling of the mineral colloids and sulphite least.

TABLE 6

Nitrogen Dissolved by Repeated Extraction

20 g. soil and 200 ml. solution	*0·2 N pyroborate*		*0·5 N pyrophosphate*		*0·5 N sulphite*	
	Cold	*Boiling*	*Cold*	*Boiling*	*Cold*	*Boiling*
First extraction						
Volume in soil residue ml. . . .	30	30	42	42	27	26
Percentage N dissolved	5·2	33·4	15·4	48·2	7·3	38·0
Second extraction						
Volume in soil residue ml. . . .	32	32	58	60	28	26
Percentage N dissolved	4·0	9·3	4·2	10·7	4·6	13·8
Third extraction						
Percentage N dissolved	3·6	3·0	3·4	2·2	2·6	2·3
Sum of N extracted %	12·8	45·7	23·0	61·0	14·5	54·2

TABLE 7

Effect of pH on Extraction of Nitrogen by Boiling Solution of 0·5 N Sodium Pyrophosphate and Sulphite

Solution	*Initial pH*	*Extract pH*	*Percentage of N extracted*
Pyrophosphate	9·9	9·5	50·2
,,	9·2	9·5	44·5
,,	8·0	8·4	37·6
,,	7·0	7·1	30·7
Sulphite	9·2	8·4	39·6
,,	10·7	9·8	51·6

Experiment 7. Effect of pH on extraction of nitrogen by boiling solutions of 0·5 N sodium pyrophosphate and sulphite

Since the pH appears to exert an overriding effect on the extraction of nitrogen a series of boiling extractions was made with the pH adjusted by addition of sodium hydroxide to the sulphite solution and of hydrochloric acid to the pyrophosphate.

The results in Table 7 show that increasing the initial pH of the sulphite solution from 9·2 to 10·7 increased the final pH of the extract to 9·8 and the percentage of nitrogen dissolved from 39·6 to 51·6. Decreasing the pH of the pyrophosphate solution from its initial 9·5 to 7·0 decreased the pH of the extracts and the percentage of nitrogen dissolved from 50·2 to 30·7. Therefore, at comparable pH values boiling pyrophosphate

and sulphite solutions dissolve about the same quantity of nitrogen from this meadow soil.

Discussion

The results of Experiment 1 show that in all the cold extractions potassium solutions were less effective than sodium solutions, but the difference between these two alkali cations was less marked with boiling treatments and, in fact, potassium oxalate and citrate dissolved slightly more than the corresponding sodium solutions. This comparison, in the absence of calcium and magnesium cations, shows that there is no advantage to be gained by using potassium salts and probably the same difference would have shown had the two been compared on the untreated calcareous soil. In those cases where potassium gave a lower extraction the difference seems to be due to its lower dispersion effect on the electronegative organic colloids while in the oxalate and citrate solutions the complexing effect of these anions with aluminium iron and possibly silicate is likely to overshadow the relative effects of the cations sodium or potassium.

Experiments 1 and 2 both demonstrate that citrate and oxalate are the most effective organic anions for extracting organic matter from a calcium-free soil and this agrees with the experience of other workers both with acid-washed and untreated soils. Considering the dicarboxylic acids, extraction of nitrogen appears to decrease as the chain length of the anion increases from oxalate to succinate, although the pH of the extracts declines also. Phthalate, which has a spatial arrangement of its carboxyl groups similar to succinate, gives almost identical extraction of the hydroxy-carboxylic acids, lactate with one hydroxyl adjacent to one carboxyl extracts less nitrogen than malate with two carboxyl groups which, in turn, is not so effective as tartrate with two hydroxyl and two carboxyl groups. The mono hydroxy-tricarboxylic citrate is slightly more effective still but not more so than oxalate.

Of the inorganic series, pyrophosphate proved the best of the salts used in Experiment 2. Hydrosulphite was as effective as fluoride and the results of Experiment 3 showed that, in the absence of calcium, boiling sulphoxylate, hydrosulphite, sulphite, and sulphide solutions all extracted about 60 per cent. of the nitrogen in the region of pH 9, so they are practically as effective as pyrophosphate. Their action would seem to be different from that of pyrophosphate in that they do not appear to form complexes with ferric iron and aluminium. The sulphoxylate, hydrosulphite, and sulphide reduced much of the ferric iron and the latter especially gave a precipitate of black ferrous sulphide which separated with the mineral soil particles on centrifuging but the sulphite produced no visible changes in the mineral matter. The sulphites of both aluminium and ferric iron have a low solubility and it would appear that the chief mechanism in the relatively high extraction of organic matter from the untreated soil by boiling is the precipitation of calcium, ferric, and aluminium sulphites or basic sulphites with release of sodium humate compounds since much less organic matter is dissolved by sodium sulphate solution of the same strength. One advantage of sodium sul-

phite solution is the fact that during boiling it maintains a fairly uniform pH between 8 and 8·4 which should not cause serious hydrolysis of the organic polymers while under these mildly alkaline conditions it preserves a reducing condition which should prevent oxidative changes in the organic matter through browning reactions. There remains the possibility that the sulphite may react with some of the humus components through aldehyde or thiol or other reactive groups and this point needs further investigation.

Experiments 5 and 6 show that preliminary extraction of the soil with sodium or potassium chloride solution to remove nitrate, and most of the exchangeable ammonium, calcium, and magnesium, had little effect on the subsequent extraction by either pyroborate, pyrophosphate, or sulphite solutions.

Repeated extraction at 18° C. failed to dissolve more than about a quarter of that dissolved by boiling for 1 hour, and this poses the question of whether some irreversible change is produced in the organic matter by boiling. The fact that extraction is increased as the pH of the solvent is raised above 7 and that the dissolved organic matter always has some calcium, aluminium, and iron associated with it suggests that the solubility of the polymeric components of the soil organic matter depends in large measure on the degree of its chelation with polyvalent metal cations. As the pH is raised the equilibrium between

is likely to be displaced to the right with consequent increase in solubility of the organic complex.

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A METHOD FOR THE MEASUREMENT OF THE CALCIUM DEFICIT IN SALINE SOILS

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Summary

The calcium deficit of a saline soil is defined as the amount of calcium which must be supplied to saturate the soil with divalent cations. A method is described whereby this amount can be measured in samples of unwashed saline soil and used to estimate the amount of gypsum needed in the field to prevent deterioration of the soil structure while it is being leached into a salt-free condition.

Introduction

WHEN a soil is inundated with saline water containing a high concentration of sodium ion, such as sea-water, an exchange reaction occurs in which the original exchangeable cations of the soil are partly replaced by sodium. If the saline solution remains in contact with the soil, equilibrium is established according to the equation

$$(Ca,Mg)\ soil + NaCl = (Ca,Mg,Na)\ soil + (Ca,Mg,Na)\ Cl.$$

The extent to which the reaction proceeds depends both on the concentration of the solution and the amount that has leached through the soil.

If such a system is then leached with fresh rain water the saline solution is displaced from the soil and the resulting decrease in salt concentration causes a rapid deflocculation and a marked decrease in permeability. Unless a divalent cation is supplied in the leaching solution to replace that removed by the saline water, some deterioration of the soil structure is inevitable. Under field conditions, the process is a combination of dilution and leaching, depending upon the natural sequence of events.

The reclamation of sodic soils by the use of saline waters containing various proportions of monovalent and divalent cations was discussed in detail by Reeve and Bower (1960) in terms of the sodium-adsorption ratio of these solutions, as defined by the expression $[Na]/\sqrt{[Ca+Mg]}$, which is directly related to the degree of sodium saturation of the soil in equilibrium with the solution. Reeve and Bower point out that when the solution is diluted the sodium-adsorption ratio tends to decrease so that the amount of exchangeable sodium in the soil decreases. This, however, does not mean that deflocculation will not take place, because the salt concentration may fall below the critical value before the sodium-adsorption ratio reaches a sufficiently low value for the soil to remain stable. Leaching in addition to dilution increases this risk considerably. As Reeve and Bower point out, this difficulty can be overcome if, instead of using fresh water, the soil is treated with a natural water that has a

sodium-adsorption ratio such that the system can be adjusted to remain within safe limits.

Where supplies of such water are not available, the same result can be produced by applications of gypsum or calcium chloride that will be washed into the soil by the rain. For such a treatment to be successful, the calcium salt must be applied before the structure has deteriorated while the saline solution still remains in the soil, because once the drainage is impeded the remedial solution will be unable to penetrate the soil. It is also desirable that estimates of the amount of gypsum needed by the soil should be based on a simple and convenient laboratory examination of samples of the soil in the condition in which it exists in the field. The experiments described in this paper were undertaken to develop a method that would provide an estimate of the minimum amount of gypsum necessary for the reclamation of such soils.

The Calcium Deficit

The method is based upon direct measurements of the amount of calcium that must be applied to the soil to restore its original state rather than on measurements of the amount of sodium in the soil. This principle was used because of the difficulty of defining the 'amount of exchangeable sodium' in a soil that contains excess salt. The amounts of the various cations present in such a soil can be measured by displacing them with an ammonium salt solution, but when the total cationic charge is larger than the exchange capacity of the soil it is impossible to state the amount of each cation that is to be regarded as associated with the exchange complex of the soil rather than as a component of the salts in the solution. Even if this division could be made it would be an unsatisfactory approach because the amount of 'exchangeable sodium' is related to the sodium-adsorption ratio of the soil solution, and since this ratio is dependent upon the total concentration it is clear that the 'exchangeable sodium' will depend upon the water content of the soil.

The amount of calcium that is taken up in resaturating the soil with divalent ion is, however, a definite quantity which may be termed the 'calcium deficit' of the soil, and it can easily be found by measuring the decrease in the calcium concentration when the soil is shaken with a solution of a calcium salt. When there is a large quantity of sodium in the soil it may be necessary to repeat this treatment several times because the high concentration of sodium in the first extract will stop the exchange reaction short of completion. This effect is shown by the data in Table 1. In this experiment, 10-g. samples of four soils of different textures, from coastal regions of south-eastern England that had been damaged by inundation with sea water, were shaken with 50-ml. aliquots of N/50 calcium chloride solution and centrifuged. A 25-ml. aliquot of the centrifugate was removed and titrated with disodium versenate, with eriochrome black T indicator, by the method of Betz and Noll (1950) to determine the total calcium and magnesium concentration in the solution.

The 25 ml. of centrifugate withdrawn was replaced with an equal volume of fresh N/50 solution, and the procedure was repeated six times.

The sodium concentration in the extracts was measured in an Eel flame photometer, and the amounts of sodium released by the soils in each treatment are presented in Table 2.

TABLE 1

The Amounts of Calcium Taken Up by Samples of Salt-Damaged Soils on Successive Shaking with Replenished $CaCl_2$ *Solution, Initially* N/50

Soil				*Calcium taken up (m.e./100 g.) in each shaking*						
No.	*Texture*	pH	$CaCO_3$ %	*1st*	*2nd*	*3rd*	*4th*	*5th*	*6th*	*Total*
1	Clay loam	7·6	5·0	1·92	0·96	0·63	0·40	0·20	0·1	4·28
2	Silt loam	7·5	12·0	0·67	0·58	0·40	0·23	0·13	0·12	2·12
3	Fine sandy loam	5·1	None	0·09	0·03	0·02	0·02	0·01	0·01	0·18
4	Sandy loam	..	..	1·95	0·25	0·10	0·07	0·04	0·03	2·44

TABLE 2

The Amount of Sodium Released from Samples of Salt-Damaged Soils on Successive Shaking with Replenished N/50 $CaCl_2$ *Solution*

	Na released (m.e./100 g.)						
Soil	*1st shake*	*2nd*	*3rd*	*4th*	*5th*	*6th*	*Total*
1	12·25	1·13	0·87	0·94	0·18	0·08	15·45
2	11·0	0·75	0·87	0·25	0·12	0·17	13·16
3	1·05	0·08	0·04	0·04	0·04	0·04	1·29
4	5·30	0·25	0·25	0·05	0·00	−0·05	5·8

The blocking effect of the high concentration of sodium in the solution on the replacement of sodium by calcium is clearly shown by these data. All the soils release between 80 and 90 per cent. of their total sodium during the first shaking period, but a much smaller fraction of the total calcium deficit is taken up at the same time. Replacement of half the solution with fresh N/50 $CaCl_2$ solution, which lowers the sodium concentration to half its former value, then permits the exchange to proceed toward completion during the second shaking period. The effect is further illustrated by the data in Table 3 which contains the results of a similar series with four specially prepared soils that contained exchangeable sodium but no excess salt. It is clear that in these soils, even when the calcium deficit is relatively large, the replacement of sodium by calcium is virtually complete during the first shaking period.

The data in Table 1 indicate that the calcium deficit of the saline soils cannot be estimated directly from the amount of calcium taken up during the first shaking period because this amount may be less than 50 per cent. of the total deficit. It is therefore clear that a routine method for the determination of the calcium deficit in which soil is shaken only once with a calcium salt will be inadequate. Any complex procedure that involves a number of separate operations is undesirable

for operational reasons, however, and a more practicable method, which is described below, was developed for use as routine procedure.

TABLE 3

The Amount of Calcium Ion Taken Up on Shaking Samples of Four Soils Containing Exchangeable Na *but No Excess Salt with Replenished* N/50 $CaCl_2$

	Ca *taken up* (*m.e./100 g.*)		
Soil	*1st shake*	*2nd shake*	*Total*
5	0·62	0·01	0·63
6	2·4	0·2	2·6
7	3·1	0·2	3·3
8	5·8	0·4	6·2

Routine Method

When a 10-g. sample of saline soil is shaken with 50 ml. of N/50 $Ca(NO_3)_2$ solution, and 25 ml. of the centrifugate from the suspension is replaced with 25 ml. of fresh solution, the calcium concentration in the new solution is brought back halfway to N/50 and the sodium concentration is halved. If we then assume that in the second shaking period the exchange will go halfway toward completion from the stage reached at the end of the first shaking period, we may carry out the following calculation.

Let the volume of disodium versenate solution equivalent to 25 ml. of N/50 $Ca(NO_3)_2$ be T, the titre of the 25 ml. of centrifugate after the first shaking be X, and that of the 25 ml. removed after the second shaking be Y. The total Ca+Mg taken up by the 10 g. of soil in the first shaking will then be $2(T-X)$. After the 25-ml. sample is replaced by fresh N/50 $Ca(NO_3)_2$ solution, the total titre of the whole 50 ml. will be $(T+X)$, so that the amount of Ca+Mg taken up by the soil in the second shaking will be $(T+X)-2Y$, which is equal to half the total which remains to be taken up after the first shaking. Then the amount of calcium plus magnesium needed for the complete exchange on the whole 10 g. of soil will be $2(T-X)+2((T+X)-2Y)$ or $4(T-Y)$, so that the total calcium deficit of the soil can be determined by measurement of Y alone. The procedure may be simplified by using a back titration procedure in which the value of $T-Y$ is obtained directly without calculation: an amount of disodium versenate equivalent to 25 ml. of N/50 $Ca(NO_3)_2$ (i.e. T ml.) is added to the 25 ml. of centrifugate removed after the second shaking and the mixture is back titrated with calcium chloride solution. The concentration of the calcium chloride solution can be adjusted so that the volume used in the back titration is equal to the calcium deficit of the soil in m.e. per 100 g.

The detailed routine procedure will then be as follows. A 10-g. sample of air-dry unwashed saline soil is shaken with 50 ml. of N/50 $Ca(NO_3)_2$ solution for 30 minutes and then centrifuged: 25 ml. of the clear centrifugate is removed with a pipette and discarded, and 25 ml.

of fresh N/50 $Ca(NO_3)_2$ is added to the soil sample. After a second shaking and centrifuging, 25 ml. of centrifugate is removed and added to a volume of standard disodium versenate solution equivalent to 25 ml. of the stock N/50 $Ca(NO_3)_2$ solution, and to the mixture is added 5 ml. of borax-sulphide buffer and 5 ml. of eriochrome Black T indicator solution. An excess of disodium versenate is indicated by the formation of a clear turquoise-blue colour. The excess versenate is determined by back titration with standard $CaCl_2$ solution, the endpoint being the first appearance of a purple tint. The back titration procedure has the additional advantage that it prevents the precipitation of magnesium hydroxide which may be formed if the alkaline borate solution is added before the sequestering versenate solution. The use of $Ca(NO_3)_2$ solution in place of $CaCl_2$ permits determination of the total Cl content of the soil.

The stock borate-sulphide buffer solution is prepared by dissolving 40 g. of $Na_2B_4O_7 \cdot H_2O$ in 800 ml. of distilled water, adding a solution containing 10 g. of NaOH and 5 g. of $NaS_2 \cdot 9H_2O$ in 100 ml. of distilled water, and adjusting the volume to 1 litre. The indicator solution contains 0·5 g. of eriochrome Black T and 4·5 g of hydroxylamine hydrochloride in 100 ml. of 95 per cent. ethanol.

In this procedure the magnesium in the soil is taken into account, since the eriochrome indicator is sensitive to both calcium and magnesium. Because the titration measures the sum of these ions, the measured calcium deficit represents the amount of calcium required to replace the sodium ions but not the magnesium. Determinations of the potassium in the four soils listed in Tables 1 and 2 showed that the potassium was negligible in comparison with the sodium.

The calcium deficits and sodium contents of soils 1–8, as measured by the routine method, are given in Table 4. Comparison of these data with those in the previous tables shows that the routine method tends to underestimate the true deficit by about 10–15 per cent. if the salt content of the soil is high. This error cannot be regarded as serious, however, because the measured deficit is only to be regarded as a minimal figure when it is used to calculate the amount of gypsum or calcium chloride needed by the soil: larger amounts must be applied in the field

TABLE 4

The Calcium Deficit and Sodium Contents of Soils 1–8 Measured by the Routine Procedure

Soil	*Calcium deficit (m.e./100 g.)*	*Sodium content (m.e./100 g.)*
1	3·8	14·5
2	1·8	12·5
3	0·15	1·2
4	2·45	5·8
5	0·64	..
6	2·6	..
7	3·5	..
8	6·6	..

to make good the inevitable loss of calcium during natural leaching, a loss that depends upon the rate of infiltration and drainage through the soil.

Effect of Leaching Saline Soils

Air-dry samples of six salt-damaged soils were placed in Büchner funnels and gently rewetted with distilled water under a tension of 10 cm. of water to prevent disruption of their crumb structures. The tension was then reduced to 2 cm. for a few hours, after which the samples were flooded with distilled water which was allowed to percolate downward until the samples became impermeable. After drying at room temperature, the calcium deficits and sodium contents of the samples were measured by the routine method. These values are compared with those obtained from the unleached soils in Table 5. Except in one soil the values of the calcium deficits in the leached soils are nearly equal to the sodium content, indicating the excess salt has been almost completely removed during the leaching. The increase in the calcium deficit indicates that significant amounts of calcium or magnesium were lost during the leaching, but there is no simple relationship between the original calcium deficit and the final state of the soil. These data show clearly that soil samples should not be washed before the measurements are made because the washing alters their condition considerably from that which would be present in the field, particularly where remedial dressings of calcium salt had been applied before serious leaching took place. The washing of numbers of samples would also be a tedious and difficult process which would be very undesirable in a routine laboratory procedure.

TABLE 5

Effect of Leaching with Distilled Water on Calcium Deficits and Sodium Contents of Salt-Damaged Soils

	Original soil		*Leached soil*	
Soil	Ca *deficit*	Na *content*	Ca *deficit*	Na *content*
9	0·2	5·25	1·1	1·1
10	2·3	7·75	2·3	3·1
11	3·3	21·0	7·0	6·8
12	2·9	18·5	6·1	6·2
13	2·0	6·25	3·3	3·1
14	0·4	16·25	5·4	5·0

Effect of Storage of Soil Samples

When a number of air-dry samples of saline soil were stored in the laboratory and re-examined after a period of several months, it was found that their calcium deficits had changed. A detailed study of a group of 23 soils from south-eastern England and 23 other soils from Holland and Belgium showed that in all except two of them the calcium deficits had decreased considerably over a period of about 6 months. The changes were variable and showed no correlation with the original

deficit, the salt content, the soil type, or the presence of calcium carbonate. In several samples the deficit changed from a positive to a negative value, indicating the production of excess calcium ion in the soil.

Owing to the lack of experimental information the mechanism of this change remains obscure, but it may be similar to that by which a damaged soil, if left undisturbed in the field, will return to a normal condition in a number of years. This process may have been accelerated by the warm and dry environment in which the samples were stored in the laboratory. Although the nature of the changes is not understood, it is clear that only fresh samples of soil, which have not been stored for more than 2 or 3 weeks, should be used for measurement of calcium deficits, and the samples should be dried at the lowest convenient temperature.

Gypsum Requirement of Field Soils

Although the calcium deficit of a salt-damaged soil can be used to calculate the minimum rate of application of gypsum for restoration of the soil to a safe condition, it cannot be used to predict the rate of recovery which is dependent upon a number of other factors such as the rate of solution of the gypsum, the efficiency of the drainage and variations in the salt content of the soil. Practical experience has shown that the routine method for the determination of the calcium deficit has proved most valuable when it was used to study the history of a damaged soil by resampling and re-examination of the treated soil at suitable intervals until it has returned to a safe salt-free condition (N. H. Pizer, 1960, private communication).

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A PARTIAL FRACTIONATION OF ALKALI-SOLUBLE SOIL ORGANIC PHOSPHATE

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Summary

A study has been made of the precipitation of soil organic phosphates from alkaline extracts. Acidification to a pH of about 0·4 or below precipitated a small and constant proportion of the extracted organic phosphate. Above pH 0·4 there was an increase in the precipitation up to a pH of about 2 to 3. The proportion of the phosphate brought down at pH 2·9 could in some cases be increased by prior addition of aluminium sulphate, but in no case did this affect the proportion precipitated at pH 0·2. There was marked precipitation of orthophosphate above pH 3, in the presence of excess aluminium, but below pH 3 it was negligible.

Inositol hexaphosphate and DNA were precipitated virtually quantitatively at pH 2·9 in the presence of added aluminium even if the extract was incubated before precipitation. Precipitation of RNA was not complete and could be prevented entirely by prior incubation of the extract. At pH 0·2 DNA was precipitated, but not inositol hexaphosphate. Less than half of a freshly purified sample of RNA was brought down, and no precipitation occurred if the RNA was allowed to stand overnight in alkaline solution before acidification.

The soil phosphate esters have been divided into three main classes: an acid-insoluble fraction precipitated at pH 0·2, and two acid-soluble fractions, one of which is precipitated at pH 2·9 in the presence of excess aluminium, while the other remains in solution. Part of the acid-insoluble fraction was readily mineralized during incubation in dilute sodium hydroxide, and some hydrolysis is likely during extraction of the soil with this solvent.

Introduction

RECENT investigations have indicated that the nature of about half of the total organic phosphate in soils is obscure. As Black and Goring (1953) have pointed out, attention has been limited mainly to a study of three classes of compounds, the inositol phosphates, ribonucleic acids and their derivatives, and phospholipids.

The presence of inositol phosphates has been indicated in many soils (Yoshida, 1940; Wrenshall and Dyer, 1941; Bower, 1949; Smith and Clark, 1951; Pedersen, 1953; Anderson, 1956) and the hexaphosphate (phytin) has been shown to account for up to one-half of the total organic phosphate (Anderson, 1956; Caldwell and Black, 1958). Other inositol phosphates are present but only in small amounts.

Bower (1949) and Sokolov (1948) estimated that the amount of nucleic acid in soil was considerable, the latter obtaining values for nucleoprotein as high as 60 per cent. of the total organic phosphate. Derivatives of ribonucleic acid (RNA) and deoxyribonucleic acid (DNA) have been identified in soil extracts or hydrolysates, but the presence of a large amount of nucleic acid or nucleotides in soil now seems doubtful since, when specific methods of identification have been employed in examining soil products (Adams *et al.*, 1954; Anderson, 1958, 1961), only small amounts have been detected.

No phospholipids have yet been isolated from soil, and there is no published evidence to suggest that such compounds are present in more than small amount.

When an alkaline soil extract is acidified, the resulting precipitate of humic acid contains a certain amount of organic phosphate. Hydrolysis of humic acid releases derivatives of DNA (Anderson, 1958, 1961), but only a small fraction of the phosphate can be attributed to this compound. Yoshida (1940) and Bower (1949) found that about 5 to 15 per cent. of the organic phosphate in a sodium hydroxide extract of soil was precipitated with humic acid, but Dyer and Wrenshall (1941) precipitated over 50 per cent. from an ammonium hydroxide extract even in the presence of oxalate. If oxalate was omitted the amount was higher and presumably contained ferric phytate. Adams *et al.* (1954) also precipitated about 50 per cent. of the organic phosphate with humic acid even though the pH of the liquid was 0·8, where ferric and aluminium phytates are usually soluble (Jackman and Black, 1951). It therefore seems probable that there are distinct differences in the nature of the phosphate esters in various soils, or that differences in inorganic constituents can have marked effects on the precipitation of these compounds even in a strongly acid medium.

The main purpose of the investigation reported here was to study the precipitation of soil organic phosphates from alkaline extracts in the hope of achieving a fractionation which would eliminate differences due to varying amounts of iron and aluminium, and to examine the behaviour of added phosphate esters during precipitation. It was hoped that the study would enable the native soil phosphates to be subdivided into a number of broad groups or categories as a first step in the further characterization of the constituents present. The possibility of estimating soil inosito phosphates by a micro-method was also investigated.

Experimental

Soils

The soils examined were acid soils, in agricultural use, and derived from basic igneous, slate, granitic, and Old Red Sandstone glacial drift.

Soil extraction

The soils were extracted with cold dilute sodium hydroxide under conditions which have been shown to remove organic phosphates almost quantitatively without appreciable dephosphorylation (Saunders and Williams, 1955).

0·5 g. soil ground to pass a 100-mesh sieve was treated with 25 ml. 0·1 N hydrochloric acid in a covered beaker on the steam-bath and stirred at intervals for 1 hour. The suspension was filtered and washed with small portions of hot acid until the volume of the filtrate was about 100 ml. and the latter, which contained negligible amounts of organic phosphate, was discarded. The paper and soil were transferred to a 250-ml. centrifuge tube and shaken overnight with 200 ml. 0·1 N sodium hydroxide at about 20° C. Then 0·5 g. sodium chloride was added with shaking, to assist clarification, and the liquid was centrifuged at 3,000

revs. per minute, for 15 minutes, or until clear. Total and inorganic phosphate in the extracts were determined colorimetrically (Truog and Meyer, 1929; Williams and Stewart, 1941).

Precipitation of soil phosphates

Suitable aliquots of soil extracts, usually from 5 to 25 ml., were treated with sulphuric acid (0·1 N, 1 N, and 5 N) to give final pH values ranging from about 4·5 down to 0·2. After standing overnight the precipitates were centrifuged, washed carefully with a small amount of water, and dissolved in 2 drops of concentrated ammonium hydroxide and 2 ml. 0·1 N sodium hydroxide. The solutions were washed into silica basins containing 0·5 ml. 12 per cent. aqueous magnesium nitrate, evaporated to dryness and ignited in a muffle furnace at 600° C. for 12 minutes. The residues, after cooling, were dissolved in hydrochloric acid and phosphate was estimated colorimetrically. Typical results are shown in Fig. 1.

At low pH values the amount of organic phosphate precipitated was small and constant. As the pH rose there was an increase in precipitation until a fairly constant level was reached again in the region of pH 2 to 3. In the case of a basic igneous soil (Fig. 1A) the level rose again above pH 3, due to co-precipitation of orthophosphate, but in a granitic soil (Fig. 1C) it rapidly fell to a negligible value.

The level of phosphate obtained at very low pH values can be regarded as that contained in the humic acid fraction of soil organic matter. At higher pH values precipitation of β-humus will occur, consisting of those compounds which are normally acid soluble but are precipitated by iron and aluminium. The inflexion in the precipitation curves at about pH 2·0 is thought to be caused by iron, and at about pH 3·0 by aluminium. The humic acid precipitates obtained at low pH values also contained iron and aluminium, but probably in complex form.

Since the granitic soil had a much lower sesquioxide content than the basic igneous soil, it was thought that the drop in phosphate precipitation above pH 3 in the former might be due to a limiting amount of sesquioxide. The precipitation tests were therefore repeated, after the addition of 2 ml. 0·2 per cent. aqueous aluminium sulphate per 10 ml. of the soil extract (Fig. 2). Total phosphate in the precipitates and inorganic phosphate in the supernatant liquids were determined.

Although the presence of aluminium had some effect on the precipitation of organic phosphate from the basic igneous soil extract, it did not noticeably increase the amount precipitated at pH 2·7–3·0. There was a marked increase in the case of the other soils, however, and above pH 3 there was now a co-precipitation of orthophosphate also. The amount of orthophosphate in solution at pH 3 was only slightly less than at pH 1·5, and added orthophosphate was quantitatively recovered from the supernatant solution at pH values up to 3·0. In no instance did the presence of aluminium have any effect on the humic acid phosphate content. Larger additions of aluminium sulphate did not further increase the precipitation of organic phosphate at pH 2·7–3·0.

It was observed that if the soil extracts were stored for some days, even at low temperature, there was a small decrease in precipitation of

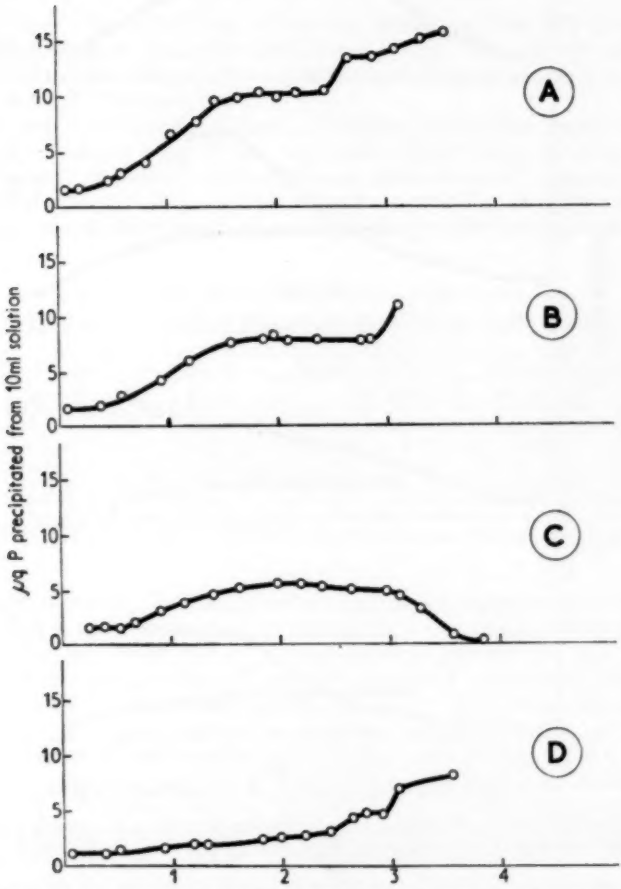

FIG. 1. Precipitation of phosphate by acidification of sodium-hydroxide extracts of soils derived from (A) basic igneous, (B) slate, (C) granitic, and (D) Old Red Sandstone drift.

organic phosphate. This was also achieved by incubation of the extracts at 37° C. for 16 hours, after which no further decrease was observed. Incubation also caused a slight increase in the amount of orthophosphate in solution.

The proportions of the alkali soluble phosphate which are precipitated at pH 0·2 and 2·9 are shown in Table 1. The precipitates obtained at pH 2·9 contained a small amount of orthophosphate, measured by the difference in the orthophosphate in solution at pH 1·5 and pH 2·9, and an appropriate correction has been made.

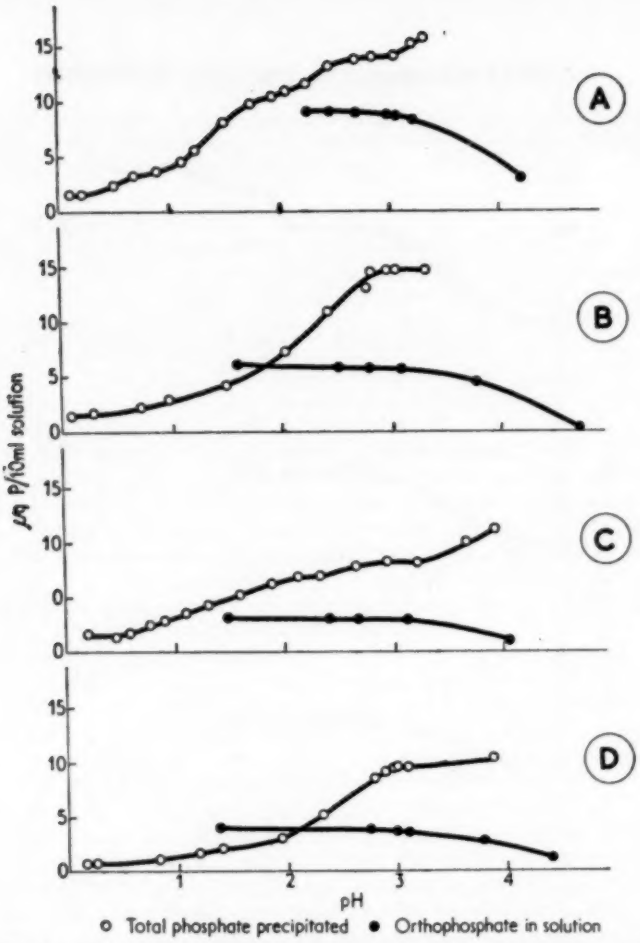

FIG. 2. Precipitation of phosphate by acidification of sodium-hydroxide extracts of soils in the presence of added aluminium sulphate. The soils are described in Fig. 1.

TABLE 1

The Precipitation of Organic Phosphates from Alkaline Soil Extracts in the Presence of Excess Aluminium

Soil		*Organic* P *precipitated* (% *extracted* P)	
No.	*Parent material, and drainage*	*pH 2·9*	*pH 0·2*
1	Basic igneous, freely drained	70	13
2	Basic igneous, poorly drained	75	19
3	Slate, freely drained	66	9
4	Granitic, freely drained	72	8
5	Granitic, poorly drained	83	16
6	Old Red Sandstone, freely drained	77	13

Precipitation of added phosphate esters with humic acid

Materials. The sodium salt of inositol hexaphosphate was prepared from a pure sample of phytin[1] (Anderson, 1956). The nucleic acids, in the form of sodium salts, were commercial products obtained from yeast (RNA) and calf thymus (DNA).

The esters were dissolved in 0·1 N sodium hydroxide to give a concentration of about 5 μg. P/ml., the exact figure being confirmed by analysis. 1-ml. aliquots of each ester were added to 5-ml. aliquots of soil extract, and precipitation was carried out by addition of sulphuric acid to give pH values of 0·2 and 2·9, corresponding to the flat portions of the

TABLE 2

Precipitation of Added Phosphate Esters from Soil Extracts

	Phosphate content of precipitates μg. P								*Phosphate added* μg. P				*Recovery in precipitate* (%)					
	pH 2·9*				*pH* 0·2						*pH* 2·9	*pH* 0·2	*pH* 2·9			*pH* 0·2		
Soil no.	*A*	*B*	*C*	*D*	*A*	*B*	*C*	*D*	*B*	*C*	*D*		*B*	*C*	*D*	*B*	*C*	*D*
1	6·5	10·5	11·6	8·0	1·3	1·1	6·5	1·3	4·0	5·7	3·2	3·2	100	89	47	−5	91	0
3	6·8	10·5	12·2	11·4	1·1	1·1	6·2	1·7	4·0	5·7	0·9	0·9	92	95	67	0	89	9
4	4·7	8·6	10·6	6·5	0·6	0·4	5·7	0·8	4·0	5·7	3·2	3·2	98	104	56	−5	89	6
6	4·6	8·4	10·2	7·6	0·8	0·8	5·9	0·9	4·0	5·7	0·2	3·2	95	98	48	0	89	3

* Aluminium sulphate added prior to precipitation.
A, no addition. *B*, *C*, and *D* represent additions of inositol hexaphosphate, DNA, and RNA, respectively, to 5 ml. extract.

precipitation curves. In the latter case aluminium sulphate solution was added prior to precipitation. After standing overnight each sample was filtered through a moist pad of washed cellulose powder (10 mm. diam., 4 mm. thick), which did not adsorb dissolved phosphate, and was washed carefully with a small quantity of water. The precipitate was dissolved in 2 drops concentrated ammonium hydroxide and 1 ml. 0·1 N sodium hydroxide, and washed into a silica basin containing 0·5 ml. 12 per cent. aqueous magnesium nitrate. The precipitation vessel was treated with 1 ml. 0·1 N sodium hydroxide to dissolve any adhering precipitate, and this solution was also transferred to the silica basin. The liquid was evaporated to dryness, ignited, and phosphate estimated.

The results are given in Table 2. At the higher pH level, precipitation of inositol hexaphosphate and DNA was almost complete but only about half of the RNA was precipitated. At pH 0·2 inositol hexaphosphate was not precipitated, and only small amounts of RNA were brought down. Nearly all of the DNA, however, was still precipitated at the lower pH.

Since commercial samples of RNA are sometimes prepared from alkaline extracts, some degradation of the product is possible. A sample was therefore purified as follows: 5 g. RNA was suspended in 150 ml. water and dilute ammonium hydroxide added, with stirring, until it had dissolved. The solution was filtered, and poured very slowly into a mixture of 300 ml. ethanol and 2 ml. hydrochloric acid with vigorous

[1] The phytin was given by Messrs. Ciba.

mechanical stirring. The resulting precipitate was washed with aqueous alcohol, suspended once more in water, and the process repeated twice. Finally it was washed with ethanol and ether, and dried.

Precipitation tests were then carried out on soil extracts to which a solution of purified RNA had been added. The results obtained with the ordinary commercial and purified samples are summarized in Table 3.

TABLE 3

Comparison of the Precipitation of Unpurified and Purified Commercial Yeast Nucleic Acid from Soil Extracts

	Recovery (% of added P)			
	Unpurified sample		*Purified sample*	
Soil no.	*pH 2·9**	*pH 0·2*	*pH 2·9**	*pH 0·2*
1	47	0	83	44
3	67	9	87	36
4	56	6	..	..
5	..	..	81	55
6	48	3	81	46

* Aluminium sulphate added prior to precipitation.

TABLE 4

Recovery of Added Phosphate Esters from Incubated Soil Extracts

	Phosphate content of precipitates μg. P						*Recovery (%)*			
	*pH 2·9**			*pH 0·2*			*pH 2·9*		*pH 0·2*	
Soil no.	*A*	*B*	*C*	*A*	*B*	*C*	*B*	*C*	*B*	*C*
1	5·9	9·9	11·1	0·8	0·7	5·9	100	91	−3	89
3	5·9	9·6	11·5	0·7	0·6	5·9	93	98	−3	91
4	4·4	8·2	9·4	0·4	0·4	5·5	95	88	0	89
6	4·0	7·8	9·0	0·5	0·8	5·8	95	88	8	93

* Aluminium sulphate added prior to precipitation.

A, no addition. *B* and *C* represent additions of inositol hexaphosphate (4·0 μg. P) and DNA (5·7 μg. P), respectively, to 5 ml. extract.

The purified sample was precipitated to a greater extent at both pH values although recovery was still low at pH 0·2, and it appears that the chain length of RNA and the pH of the medium are both of critical importance in governing its precipitation from soil extracts. This was further substantiated in an experiment in which soil extracts with purified RNA added were allowed to stand at room temperature overnight before precipitation was carried out, reducing precipitation to 14 per cent. at pH 2·9 and 0 per cent. at pH 0·2. Mononucleotides of RNA, obtained by incubation of RNA in 0·1 N sodium hydroxide, were not precipitated at either pH level.

Incubation had no marked effect on the precipitation of inositol hexaphosphate and DNA from soil extracts (Table 4).

Hydrolysis of humic acid phosphate

It was observed that when humic acid precipitates were dissolved in alkali, and the solutions incubated, a small amount of orthophosphate was released.

The precipitates, prepared by acidifying 50 ml. aliquots of soil extract to pH 0·2 were washed with water, and redissolved in 10 ml. 0·1 N sodium hydroxide. The solutions were incubated at 37° C. for 24 hours, the humic acid was reprecipitated with N sulphuric acid and removed by centrifuging, and orthophosphate was determined in the supernatant liquids. The total phosphate was determined in humic acid precipitates which had not been incubated.

Estimation of inositol phosphate, and DNA

Total soil inositol phosphates were determined by a chromatographic method (Anderson, 1956). The purines and pyrimidines in humic acid were determined and the corresponding polynucleotide phosphate was calculated (Anderson, 1961).

Discussion

In fractionation studies of soil organic matter, the terms humic acid, fulvic acid, and β-humus have been used a great deal, but are frequently criticized since the mode of preparation of each fraction is often ill defined, and there are many distinct substances present in them.

The organic phosphates precipitated by the acidification of alkaline soil extracts are of two distinct types, those which are inherently insoluble due to their organic chemical structure and those which give a soluble anion in pure acid solution but are precipitated in the presence of sesquioxides. The behaviour of the soil phosphate esters therefore runs parallel with that of the whole 'organic matter', and a convenient initial fractionation can be based on the separation of the alkali soluble organic matter into the traditional categories, provided the conditions of precipitation are precisely defined, and suited to the properties of the phosphate esters.

In a group of Scottish agricultural soils of differing origin, it was found that the presence of sesquioxides had no apparent effect on precipitation below a pH of about 0·4, and that a small and constant proportion of the total organic phosphate was insoluble below this pH. Added DNA and a proportion of RNA of high molecular weight were precipitated in this humic acid fraction while inositol hexaphosphate, a partially degraded sample of RNA, and mononucleotides remained soluble. It was shown that RNA was soon degraded in 0·1 N sodium hydroxide even at normal temperature and is unlikely to be precipitable after overnight extraction with this solvent. Part of the humic acid phosphate, possibly phosphoprotein, was readily mineralized during incubation in alkaline solution (Table 5). This category of phosphate was no doubt partially hydrolysed during extraction of the soil, and therefore present in greater quantity than indicated.

Inositol hexaphosphate was almost quantitatively precipitated at pH

values about 2·7 to 3·0 and the phosphate precipitation curve tends to flatten out in this region. Precipitation of orthophosphate occurred slightly above pH 3, and pH 2·9 was finally selected as being most suitable for the separation of the sesquioxide precipitable organic phosphate. This category can be measured by the difference between the organic phosphate precipitated at pH 2·9 and 0·2, on the assumption that humic acid phosphate is insoluble at both pH values.

The remaining organic phosphates, which are acid soluble at pH 2·9 even in the presence of sesquioxide, will include mononucleotides and polynucleotides of limited molecular weight. A small proportion of this fraction may be insoluble at higher pH values in the presence of sesquioxide, and this aspect is being investigated further.

TABLE 5

Fractionation of Soil Organic Phosphate

	Phosphate in fraction											
	Acid insoluble (humic acid)						*Acid soluble (fulvic acid)*					
							Precipitated by sesquioxide at pH 2·9				*Not precipitated*	
	Total		*Polynucleotide*		*Alkali labile*		*Total*		*Inositol phosphates*		*Total*	
Soil no.	*a**	*b*†	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
1	89	12·7	6	0·9	20	2·9	398	56·9	328	46·9	212	30·3
2	53	19·3	6	2·2	11	4·0	152	55·3	114	41·5	70	25·5
3	71	8·7	19	2·3	23	2·8	467	57·5	319	39·3	274	33·8
4	40	7·6	6	1·1	8	1·5	336	64·1	188	35·9	148	28·3
5	68	16·0	11	2·6	9	2·1	286	67·4	105	24·8	70	16·5
6	59	12·5	6	1·3	9	1·9	304	64·4	192	40·7	109	23·1

* *a*, p.p.m. P in soils. † *b*, % extracted organic P.

The distribution of the organic phosphate of several soils in the various categories is shown in Table 5. From 8 to 19 per cent. of the extracted organic phosphate was associated with the humic acid fraction, and a further 55 to 67 per cent. was precipitated at pH 2·9 in the presence of excess aluminium. The remainder, from 16 to 34 per cent. of the extracted phosphate, was acid soluble. In all cases the sesquioxide precipitable organic phosphate exceeded the amount of inositol phosphates determined by a chromatographic method showing that the fraction contained at least one other ester. As a result, such a fractionation cannot be used as a micro-method of determining soil inositol phosphates.

The properties shown by the soil phosphate esters in this study have enabled them to be classified into three main categories and will provide a basis for more detailed qualitative analysis of the compounds present. Already a large part of the sesquioxide precipitable phosphate has been characterized as inositol phosphate, and DNA or related polynucleotides have been identified in the humic acid fraction, but much of the humic and fulvic acid phosphate is as yet of unknown character.

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THE FATE OF SOLUBLE PHOSPHATE APPLIED TO SOILS

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Summary

It is commonly known that the soluble phosphate added to soils is largely changed into iron and aluminium phosphates in acid soils, and into calcium phosphate in calcareous soils. Recently Chang and Jackson (1957*a*) employed a method to fractionate the inorganic soil phosphorus into four principal forms, namely, aluminium phosphate, iron phosphate, calcium phosphate, and occluded phosphate, enabling more detailed examination of the fate of applied phosphate to be made using the method of Chang and Jackson (1958). The purpose of this investigation is to study the fixation and transformation of soluble phosphate added to soils of different characteristics under different conditions.

Materials and Methods

Six contrasting soils, listed in Table 1, were used to study the fixation and transformation of added soluble phosphate under different moisture

TABLE 1

General Properties of the Experimental Soils

Soil location	*Soil group*	*Soil texture*	*Clay content* %	pH	*Inorganic* P, *p.p.m. as*			*Total*
					Al-*phos.*	Fe-*phos.*	Ca-*phos.*	
Taipei	Sandstone and shale alluvial soil (University farm, heavily fertilized)	Silty clay loam	..	5·3	328	260	49	637
Meolee	Sandstone and shale alluvial soil	Sandy loam	17·5	6·3	35	25	31	91
Taoyuan	Latosol	Clay	53·6	5·5	35	106	27	168
Chunglee	Latosol	Silty clay	48·3	5·3	20	63	9	92
Yuanglin	Calcareous slate alluvial soil	Silty clay loam	35·2	7·5	17	29	378	424
Silay	Calcareous slate alluvial soil	Silty clay loam	..	6·5	58	60	323	441

conditions. The following three series of experiments were carried out on each soil:

1. Four portions of 50 g. of air-dry soil were placed in four small beakers. To each beaker 20 ml. of KH_2PO_4 solution, concentration 500

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p.p.m. P, were added to assure complete wetting, giving 200 p.p.m. P and 40 per cent. moisture in the soil. The moist sample was then immediately exposed to sunlight to decrease the moisture content to approximately 30 per cent. Two of the four portions were kept for 3 days and the other two portions for 100 days at this moisture content. The soil was then dried in the sun. After grinding and mixing, 1 g. of soil was taken from each beaker for phosphorus fractionation.

2. Twenty millilitres of KH_2PO_4 solution, concentration 500 p.p.m. P, were added to 50 g. of air-dry soil in small beakers. The mixture was allowed to stand overnight and was then flooded. The soil was kept flooded for 100 days before drying. One gram of each soil was taken for fractionation.

3. To 6 g. of each of the six soils, 30 ml. of KH_2PO_4 solution, concentration 40 p.p.m. P, were added and shaken for 3 hours. The added P is equivalent to 200 p.p.m. of the soil. The soil suspension was filtered off, the soil dried in the sunlight, and 1 g. taken from each sample for fractionation.

In addition, samples from two replicated plots of a long-term fertilizer experiment were fractionated in order to investigate the fixation and transformation of added soluble phosphate over a long period. The experiment, originally laid out to study the effect of the continued application of fertilizers, included twelve treatments. Samples were taken only from the plots with the following three treatments relevant to this investigation: 95 kg./ha. N as ammonium sulphate, 95 kg./ha. N, P_2O_5 and K_2O each as ammonium sulphate, calcium superphosphate, and potassium sulphate respectively for each crop, and 560 kg./ha. CaO as quicklime in addition to the fertilizers applied in the second treatment. The fertilizers were given to each crop and the samples were taken after 58 crops had been grown in 31 years, the field having been fallow for two years.

Throughout the investigation, the soils were extracted with 0·5 N neutral ammonium fluoride solution to determine the aluminium phosphate (Chang and Jackson, 1957*a*). Fife (1959*a* and *b*) has recently proposed the use of an alkaline ammonium fluoride solution and 16 hours' extraction to obtain a better selective delineation of aluminium phosphate. However, examination of a number of representative soils of Taiwan showed that the pH of ammonium fluoride solution in the range 7·0–8·5 does not materially affect the amount of phosphorus extracted. Prolonging the extraction time from 1 hour to 16 hours caused an increased dissolution of iron phosphate (Liaw, 1960).

Experimental Results

The results in Tables 2 to 5 show that the added phosphate in soils kept at field moisture capacity for 3 days (Table 2) is almost completely recovered as soluble, aluminium, iron, and calcium phosphates. Of the latter three forms of phosphate, aluminium phosphate is the most abundant in all six soils. Only in the two latosols is the amount of iron phosphate comparable with that of aluminium phosphate. Little calcium phosphate is formed even in the calcareous soils.

TABLE 2

Fixation of added 200 p.p.m. of Phosphorus in Soils at Field Moisture Capacity, 3 Days after Treatment

Soils		*Net increase of* P *in each form, p.p.m.*				*Total* P *recovered, p.p.m.*
		P *soluble in* N NH_4Cl	Al-P	Fe-P	Ca-P	
Taipei silty clay loam	A	0	164	34	1	199
	B	0	148	34	14	196
	Aver.	0	156	34	8	198
Meolee sandy loam	A	54	99	30	12	195
	B	53	101	33	4	191
	Aver.	54	100	32	8	193
Taoyuan clay	A	32	89	82	5	208
	B	14	89	83	7	193
	Aver.	23	89	83	6	201
Chunglee silty clay	A	13	94	62	25	194
	B	16	90	63	24	193
	Aver.	15	92	63	25	194
Yuanglin silty clay loam	A	27	93	67	17	204
	B	26	91	63	17	197
	Aver.	27	92	65	17	201
Silay silty clay loam	A	20	113	46	27	206
	B	27	114	46	13	200
	Aver.	24	114	46	20	203

Note: A and B refer to two replicated samples.

If the soils are kept at field moisture capacity for 100 days (Table 3) more iron phosphate is formed, while the amounts of both aluminium and calcium phosphates decrease. In the two latosols, the amount of iron phosphate even surpasses the aluminium phosphate. The changes of aluminium and calcium phosphates to iron phosphate from 3 days to 100 days are very clear.

The added phosphate fixed in soil suspension for 3 hours (Table 4) indicates that the two latosols fix phosphate more strongly than the other soils. Of the fixed phosphates, iron phosphate is higher than aluminium phosphate in five of the six soils; calcium phosphate being the least.

When the soils are kept flooded for 100 days (Table 5), the added phosphate is almost completely recovered in all but the two latosols. The loss of the added phosphate in the latosols may be due to occlusion by iron oxide during drying after flooding. The recovered phosphate is mostly fixed as iron phosphate, particularly in the two latosols. In comparison with the amounts of the three forms of phosphates fixed at field moisture capacity for 3 days, the magnitude of change from aluminium and calcium phosphates to iron phosphate is even more significant.

TABLE 3

Fixation of added 200 p.p.m. of Phosphorus in Soils at Field Moisture Capacity in 100 Days

Soils		*Net increase of* P *in each form, p.p.m.*					*Differences from* P *fixed in three days, p.p.m.*			
		P *soluble in* NH_4Cl	Al-P	Fe-P	Ca-P	*Total* P *recovered p.p.m.*	P *soluble in* NH_4Cl	P *as* Al-P	Fe-P	Ca-P
Taipei silty clay loam	A	0	134	86	1	221	0	−22	+52	− 7
	B	0	134	90	0	224	0	−22	+56	− 8
	Aver.	0	134	88	1	223	0	−22	+54	− 8
Meolee sandy loam	A	48	96	56	8	208	− 6	− 4	+24	− 2
	B	43	95	61	4	203	−11	− 5	+29	− 4
	Aver.	46	96	59	6	206	− 9	− 5	+27	− 3
Taoyuan clay	A	0	56	94	1	151	−23	−33	+11	− 5
	B	0	58	91	2	151	−23	−31	+ 8	− 4
	Aver.	0	57	93	2	151	−23	−32	10	− 5
Chunglee silty clay	A	4	72	85	10	171	−11	−20	+22	−15
	B	5	69	87	8	169	−10	−23	+24	−17
	Aver.	5	71	86	9	170	−11	−22	+23	−16
Yuanglin silty clay loam	A	35	80	76	14	205	+ 8	−12	+11	− 3
	B	29	84	73	23	209	+ 2	− 8	+ 8	+ 6
	Aver.	32	82	75	19	207	+ 5	−10	+10	+ 2
Silay silty clay loam	A	16	87	87	25	215	− 8	−27	+41	− 5
	B	19	78	90	20	207	− 5	−36	+44	0
	Aver.	18	83	89	23	211	− 7	−32	43	− 3

TABLE 4

Fixation of added 200 p.p.m. of Phosphorus in Soil Suspension (Solid : Solvent, 1 : 5), 3 Hours after Treatment

Soils	P *remaining in soln., p.p.m.*	*Net increase of* P *in each form, p.p.m.*			*Total* P *recovered p.p.m.*
		Al-P	Fe-P	Ca-P	
Taipei silty clay loam	48	87	75	2	212
Meolee sandy loam	118	32	40	5	195
Taoyuan clay	2	77	122	1	202
Chunglee silty clay	3	85	92	8	188
Yuanglin silty clay loam	63	58	69	10	200
Silay silty clay loam	76	45	67	20	208

TABLE 5

Fixation of added 200 p.p.m. of Phosphorus under Waterlogged Condition in 100 Days

Soils		*Net increase of P in each form, p.p.m.*					*Difference from P fixed in 3 days, p.p.m.*			
		P *soluble in* NH_4Cl	Al-P	Fe-P	Ca-P	*Total P recovered p.p.m.*	P *soluble in* NH_4Cl	P *as* Al-P	Fe-P	Ca-P
Taipei silty clay loam	A	0	47	167	− 3	211	0	−109	+133	−11
	B	0	47	165	− 5	207	0	−109	+131	−13
	Aver.	0	47	166	− 4	209	0	−109	+132	−12
Meolee sandy loam	A	14	117	72	− 2	201	−40	+ 17	+ 40	−10
	B	19	116	63	− 1	197	−35	+ 16	+ 31	− 9
	Aver.	17	117	68	− 2	199	−38	+ 17	+ 36	−10
Taoyuan clay	A	0	38	112	− 2	148	−23	− 51	+ 29	− 8
	B	0	36	112	− 1	147	−23	− 53	+ 29	− 7
	Aver.	0	37	112	− 2	148	−23	− 52	+ 29	− 8
Chunglee silty clay	A	0	21	119	8	148	−15	− 71	+ 56	−17
	B	0	21	117	10	148	−15	− 71	+ 54	−15
	Aver.	0	21	118	9	148	−15	− 71	+ 55	−16
Yuanglin silty clay loam	A	9	92	72	10	183	−18	0	+ 7	− 7
	B	8	92	72	15	187	−19	0	+ 7	− 2
	Aver.	9	92	72	13	185	−19	0	+ 7	− 5
Silay silty clay loam	A	18	78	93	3	192	− 6	− 36	+ 48	−17
	B	16	79	94	6	195	− 8	− 35	+ 49	−14
	Aver.	17	79	94	5	194	− 7	− 36	+ 49	−16

The amounts of calcium phosphate, aluminium phosphate, and iron phosphate of the soils from the long-term fertilizer experiment are listed in Table 6. The increases of the phosphates in various forms due to the application of superphosphate for 31 years was calculated by subtracting the amount of each form of phosphate in the soil treated with ammonium sulphate only from that treated with superphosphate. Although the phosphorus content of the crop from the later treatment might be higher, the difference in phosphorus retained in the soils may not be greatly influenced by crop removal, since the yield of rice from the ammonium sulphate plot is comparable with those from the other plots.[1]

The data show that the phosphate is mostly retained as iron phosphate, particularly in the subsoil. Aluminium phosphate is next in abundance and calcium phosphate least, the application of lime only increasing it insignificantly. The increase in occluded phosphate is insignificant and is in agreement with that reported by Dean (1938), and Chang and Jackson (1958) with regard to upland soils. The overall results are

[1] Unpublished data.

TABLE 6

Inorganic Phosphorus Fractions in Variously Treated Soils from Field Plots

Treatment		P *as* Al-*phos.* *p.p.m.*			P *as* Fe-*phos.* *p.p.m.*			P *as* Ca-*phos.* *p.p.m.*			P *as occluded* P *p.p.m.*
		Plot 1	*Plot 2*	*Aver.*	*Plot 1*	*Plot 2*	*Aver.*	*Plot 1*	*Plot 2*	*Aver.*	*Plot 1*
Ammonium sulphate only	A*	15	14	15	31	24	28	30	27	28	105
	B	10	11	11	40	24	32	23	23	23	109
Complete inorganic fertilizers	A	167	105	136	129	81	105	88	73	80	120
	B	174	100	137	296	213	255	94	59	77	85
Complete inorganic fertilizers and lime	A	125	97	111	104	89	97	100	111	106	125
	B	113	134	124	359	138	249	65	68	67	132

* A and B refer to surface soil and subsoil respectively.

similar to those found in the Almena silt loam (Chang and Jackson, 1958) and to those from soils treated in the laboratory during this investigation.

The total phosphate retained in the first foot of soil, calculated on the basis of 4,000 tons per hectare, is about 60 per cent. of that added, assuming little applied phosphate is accumulated in an organic form (Table 7). The phosphate in flooded soil, therefore, seems more mobile than that in the upland soils into which applied phosphate penetrates with difficulty. This is possibly due to the greater accumulation of iron phosphate in flooded soil and the greater mobility of the iron in the reduced condition.

TABLE 7

The Amount of Phosphate in Different Forms Accumulated in Soils in 31 Years

Treatment		P *accumulated as*			*Total*	
		Al-*phos.* *p.p.m.*	Fe-*phos.* *p.p.m.*	Ca-*phos.* *p.p.m.*	P, *p.p.m.*	% *of that applied**
Complete inorganic fertilizers	Surface soil	121	77	52	250	60
	Subsoil	126	223	54	403	
Complete inorganic fertilizers and lime	Surface soil	96	69	78	243	56
	Subsoil	113	217	44	374	

* Total amount of P_2O_5 applied in the past 31 years is 5,510 kg./ha. equivalent to 552 p.p.m. of P in the top foot of soil weighing 4,000,000 kg.

General Discussion

The data in Tables 2 to 5 clearly show that over comparatively short periods and in relatively dry soil, added soluble phosphate is mainly fixed as aluminium phosphate followed by iron phosphate, and then by calcium phosphate, regardless of the pH of the soil. When the time of contact is prolonged, the amount of iron phosphate increases and the amounts of aluminium and calcium phosphates decrease accordingly. The rate of change increases with the moisture content of the soil.

The results suggest that the first step in the reaction of soluble phosphate with the various cations occurs on the surface of the solid phases

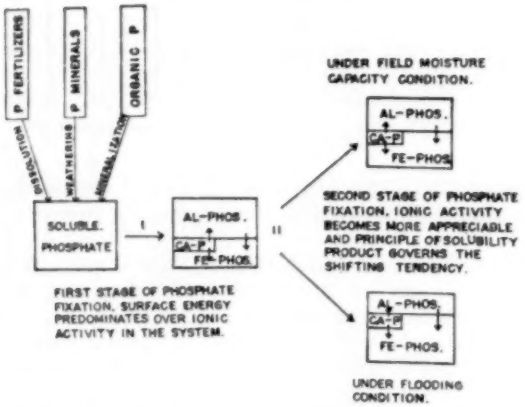

FIG. 1. Fixation and transformation of phosphate in soils.

with which the phosphate comes in contact, so that it is not the relative ionic activities of aluminium, iron, and calcium in the soil solution, but rather the specific surface area of the solid phases associated with aluminium, iron, and calcium ions that determines the relative amounts and kinds of phosphates formed. The clay fraction is the main site of phosphate fixation. In the clay the content of aluminium is much higher than that of either iron or calcium. Therefore, the added soluble phosphate is most likely to be fixed as aluminium phosphate and iron phosphate rather than as calcium phosphate in the initial stage of the reaction. As time elapses, the two former phosphates would change to the less soluble iron phosphate according to the principle of the solubility product (Chang and Jackson, 1957*b*). Since soil is a hetereogeneous system and the mobility of the ions in soil moisture is also rather restricted, owing to the reduced solvent action of bound water (Buehrer and Rose, 1943), the rate of change is slow and increases with the moisture content of the soil.

The course of fixation of added soluble phosphate in the soil is shown diagrammatically in Fig. 1.

Conclusions

It was found experimentally that the added soluble phosphate in six soils, with pH ranging from 5·3 to 7·5, kept at field moisture capacity for 3 days is mainly fixed as aluminium phosphate, followed by iron phosphate and calcium phosphate. After keeping under the same conditions for 100 days, the amount of iron phosphate increases while that of the aluminium and calcium phosphate decreases. In two latosols the amount of iron phosphate surpasses that of aluminium phosphate. Under flooded conditions for 100 days, iron phosphate becomes the dominant form of phosphate fixed in all six soils. In a soil suspension, the soluble phosphate fixed in 3 hours is dominantly iron phosphate in five of the six soils.

It was also found that the superphosphate applied to a soil over 31 years is mostly retained in the form of iron phosphate, with aluminium phosphate next, and that least is retained as calcium phosphate. Liming did not significantly change the distribution pattern.

The data suggest that the first stage of fixation of the added soluble phosphate by the various cations would occur on the surface of the solid phases with which the phosphate comes in contact, and that the relative amounts and kinds of phosphates formed would depend on the specific surface area of the solid phases associated with aluminium, iron, and calcium. In time the aluminium and calcium phosphates then gradually change to the less soluble iron phosphate, the rate of transformation increasing with the moisture content of soil.

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THE ISOMORPHOUS REPLACEMENT OF IRON BY ALUMINIUM IN SOIL GOETHITES

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Summary

It was possible to obtain relatively pure goethites ($< 2\ \mu$) from a range of soils by dissolving the clay minerals in boiling NaOH. The goethites were analysed chemically and studied by X-ray diffraction. All goethites contained aluminium, the amount ranging from 15 to 30 mol. per cent. AlOOH. The (111) spacing decreased steadily with increasing aluminium content. A study of different particle sizes from one soil showed that the aluminium content increased with decreasing particle size, and the (111) spacing showed a corresponding decrease. Extraction of soil goethite by free-iron removal agents, such as dithionite, brought into solution that aluminium contained in the goethites. The ease with which the goethite was dissolved by such treatments was inversely related to the amount of aluminium in the goethite, and led to the surprising situation in one soil where the coarser goethite was more easily extracted than the fine goethite. Measurements of the (111) spacings of many other soil goethites showed that almost invariably the unit cell dimensions were lower than those of pure goethite, indicating aluminium to be a very common replacement for iron in soil goethites. The degree of substitution of aluminium for iron probably depends on the weathering conditions in the soil. The aluminium probably restricts the size to which the goethite crystals can grow; it may, by its influence on particle size and by changing the composition of the goethite, alter the colour of goethite; it could modify the phosphate-fixing power and other chemical properties of soil goethites.

Introduction

EXTENDED observations in this laboratory have shown that the X-ray interplanar spacings of goethites in soils are lower than those of standard mineral goethites. It is also observed that some soil goethites are not readily dissolved during conventional treatments for removing free iron oxides, some often remaining after several treatments. Furthermore, relatively large amounts of aluminium are commonly dissolved along with the free iron oxides during treatments designed specifically for the solution of iron. The last observation suggests that the presence of aluminium in goethite could account for the above anomalies, especially since Correns and Engelhardt (1941) noted that oolitic goethite containing aluminium gave smaller unit cells than normal.

Methods

Sample preparation

The soils were dispersed with NaOH and particle size[1] separations were made at 2, 5, and 20 μ by sedimentation under gravity. Separations at 0·5 μ were made using a Sharples super centrifuge. The samples

[1] The particle sizes correspond to equivalent spherical diameters of clay with a density of 2·65. For goethite, density 4·3, the e.s.d. will be reduced by a factor of 1·4, i.e. the sizes will be 1·4, 3·6, 14, and 0·36 μ.

were flocculated with NaCl, washed free of chloride with water and alcohol, and dried at 100° C. It is essential that no chloride remains, as the subsequent treatment with NaOH precipitates sodalite,

$$3(Na_2Al_2Si_2O_8)2NaCl,$$

in its presence. To remove the clay minerals the clays were boiled in 5 N NaOH (usually 2 g. clay to 100 ml.) for periods from 30 to 60 minutes. The residues were washed first with water then cold 0·5 N HCl, and dried from alcohol.

Free iron removal

Free iron oxides were removed by the sodium dithionite reduction technique revised by Mackenzie (1954). In this treatment, a suspension of 100–200 mg. of clay in 20 ml. H_2O was heated to 60° C., and 1 g. of sodium dithionite was then added with constant stirring. After heating at this temperature for a further 30 minutes, the suspension was centrifuged and the supernatant liquor decanted into a 400 ml. conical beaker. The residue was washed with 0·1 N HCl and the washing was added to the beaker. The treatment was then repeated, and in some cases for a third or fourth time. Iron and aluminium determinations were then carried out on the extracts, which were either combined or kept separate depending on the aim of the analysis. No buffer was used in these extractions because some buffers are themselves capable of removing aluminium from clays (Saunders, 1959).

Estimation of iron and aluminium[1]

Ten ml. of pure 100 vol. H_2O_2 was added to each of the free iron extracts which were then boiled for 5 minutes to destroy any remaining dithionite and to oxidize any colloidal sulphur that may have formed. (Excess boiling causes hydrolysis and the precipitation of a very fine grained hydrated iron oxide.) On cooling, 1 g. NH_4Cl was added to the extracts and the group 3 hydroxides precipitated with 1 : 1 NH_4OH using methyl-red as an indicator. The excess NH_4OH was boiled off, and on cooling, the extracts were filtered through sintered glass filters. The precipitates were washed with water and the filtrates were checked for the absence of iron.

The precipitates were then dissolved in hot 0·5 N H_2SO_4 into 50 ml. volumetric flasks and made up to volume with this acid. Iron was determined on the solutions with a fluorescent X-ray spectrograph. Using 0·2 ml. of prepared standard solutions a linear relationship was found between the fluorescent intensity and concentration of iron up to 5 mg./ml. Amounts of aluminium less than a third of the iron in solution did not affect the calibration. The concentration of iron in the unknown sample was kept below 5 mg./ml.

[1] The methods described are not necessarily the simplest which could have been used. The R_2O_3 was precipitated as in certain other work it was desired to weigh the precipitate. It has been suggested that evaporation with concentrated H_2SO_4 would be a simpler way of converting the dithionite extract to a sulphate. Iron could have been determined directly on the dithionite extract by X-ray spectrography.

To remove the iron prior to aluminium determinations, 25-ml. aliquots were electrolysed using a Pt wire anode and a mercury pool cathode, passing 2 amperes for 2 hours. The supernatant liquor was withdrawn with a pipette and added to 100-ml. volumetric flasks. The electrodes were washed five times with distilled water and the washings were added to the flasks which were then made up to volume with water. Aluminium was determined on each solution by colorimetry using Alizarin red S as indicator (Bond, 1957).

X-ray techniques

Mineralogical examination of the clays and residues was carried out using X-ray diffraction powder cameras of 5·73 and 19 cm. diameter. The spacing of the (111) goethite line was measured using a Norelco high angle diffractometer with pure $PbNO_3$ added to the goethite as an internal standard. The diffractometer was made to oscillate backwards and forwards four times over the (111) line of goethite and the (311) line at 2·370 Å. of $PbNO_3$ (Swanson *et al.*, 1955), using a chart recorder. The time constant of the integrating circuit and the scanning speed of the diffractometer were adjusted so as not to produce any significant broadening or displacement of the diffraction peaks. Each goethite line was measured relative to the (311) $PbNO_3$ peak and the mean of the four estimates was taken. The standard deviation in measuring each peak was found to be 0·0004 Å. Absolute errors could be greater than this because the centres of broad diffraction lines are difficult to locate.

The (111) line of goethite was used for several reasons:

1. The position of this line is sensitive to changes in all the unit cell dimensions.
2. It is the second strongest goethite line and can therefore be measured even when goethite is present in only small amounts.
3. This line can generally be observed in the presence of clay and other oxides. The stronger goethite line at 4·15 Å. commonly coincides with clay lines while the third most intense line at 2·67 Å. is too close to the 2·69 Å. line of hematite.

Results

Table 1 shows the soils used in this study, and Table 2 gives the mineralogy of the clay fractions of these soils. Soils were chosen in which kaolin was the dominant clay mineral and, except for P 1027, goethite was the only observable free oxide or hydroxide of iron or aluminium. By using clays of high kaolin content it was possible to concentrate the goethites sufficiently, by NaOH digestion, for a detailed study of their chemistry and diffraction patterns. The efficiency of the alkali attack is shown by the high goethite content after the treatment (Tables 2 and 3), and by the almost complete removal of identifiable clay minerals even in the residues from the dithionite treatment (Table 2). The NaOH digestion does not attack the iron oxide minerals. Only 2 per cent. of the total iron was removed from H 165 during the treatment.

TABLE 1

Locations and Types of Soils from which Goethite was Extracted

Sample no.•	*Depth in.*	*Great soil group*	*Location*
BS 29	21–32	Lateritic	Western Australia
H 165	54–60	Krasnozem	Tasmania
19264	6–15	Red earth	Queensland
A 708	22–25	Yellow podzolic	Victoria
P 1027	6–12	Red-brown podzolic	Western Australia
A 543	16–22	Yellow podzolic	South Australia

• C.S.I.R.O. Division of Soils Number.

TABLE 2

Mineralogy of the Clays before and after Chemical Treatments

	Mineralogy of $< 2\ \mu$ *fraction*					
Sample	*Before treatment*		*After* NaOH *attack*		*After* NaOH *and dithionite*• *treatment*	
BS 29	Kaolin	much	Goethite	much	Goethite	little
	Goethite	much	Quartz	trace	Quartz	much
	Quartz	trace	Anatase	trace	Anatase	trace
	Gibbsite	little	Rutile	trace	Rutile	trace
			Unidentified clay	trace	Mica	trace
H 165	Kaolin	much	Goethite	much		
	Goethite	moderate	Quartz	trace		
19264	Kaolin	much	Goethite	much	Quartz	little
	Goethite	moderate	Quartz	trace	Anatase	much
	Quartz	trace				
A 708	Kaolin	much	Goethite	much	Goethite	trace
	Goethite	moderate	Quartz	trace	Quartz	moderate
	Quartz	trace	Anatase	trace	Anatase	little
			Mica	trace	Rutile	little
					Mica	much
P 1027	Kaolin	much	Goethite	much	Quartz	trace
	Goethite	v. little	Quartz	trace	Anatase	v. little
	Quartz	v. little	Hematite	much	Mica	much
	Mica	v. little	Mica	little	Talc	trace?
	Vermiculite	v. little			Vermiculite	trace?
	Hematite	v. little				
A 543	Kaolin	much	Goethite	moderate	Goethite	trace
	Mica	much	Muscovite	much	Quartz	trace
	Goethite	little			Muscovite	much

• Residue after three dithionite treatments, each for 30 minutes.

The soil goethite concentrates, i.e. the clays after NaOH attack, were extracted with dithionite; the analyses of these extracts for iron and aluminium are given in Table 3. Considerable amounts of aluminium were removed along with the iron during the dithionite treatment, and it seems probable that the aluminium comes from the goethite. The preliminary NaOH digestion would have removed any other aluminium which would normally be susceptible to the less severe dithionite extraction.[1] In any case, no other aluminium-bearing minerals could be detected in most of the clays after the NaOH treatment.

TABLE 3

Chemical Compositions and (111) Spacings of Goethites and Diaspore*

Sample (< 2 μ)	*Dithionite extraction*		*Composition of goethite mol. fraction*		d_{111} Å.
	Fe_2O_3%	Al_2O_3%	FeOOH	AlOOH	
BS 29 (NaOH)	58·3	6·36	0·855	0·145	2·436
H 165 (NaOH)	59·8	13·8	0·735	0·265	2·426
H 165 (NaOH)	58·2†	13·2†	0·738†	0·262†	
H 165	13·4	3·48	0·712	0·288	2·426
19264 (NaOH)	41·8	6·23	0·811	0·189	2·431
A 708 (NaOH)	45·4	7·46	0·795	0·205	2·431
P 1027 (NaOH)	61·0	6·53	0·856	0·144	2·433
A 543 (NaOH)	25·9	3·66	0·818	0·182	2·427
Ferrite yellow (pigment of unknown origin)	81·4	0·45	0·992	0·008	2·451
Mineral goethite (< 5 μ)	..	..	1·0‡	0	2·449
Mineral diaspore (< 5 μ)	..	..	0	1·0‡	2·318

* Iron and aluminium extracted by 3 dithionite treatments unless stated otherwise. Mn was less than 0·05 per cent. in all samples except H 165 which contained 0·18 per cent.

† Digestion in 6 N HCl. ‡ Assumed pure.

Columns 4 and 5 of Table 3 show the molar compositions of the goethites assuming all the iron and aluminium in the dithionite extracts originated from the goethite.

It is of interest that a HCl digestion removed about the same amounts of iron and aluminium from H 165 as the dithionite treatment (Table 3) and an extraction by dithionite of the untreated clay (i.e. before NaOH attack) removed almost the same relative amounts of iron and aluminium.

The (111) spacings of the goethites are given in the last column of Table 3. All the soil goethite spacings are significantly lower than that of pure goethite. Spacings measured before and after the NaOH treatments were the same. Fig. 1 shows the dependence of the (111) soil goethite spacing on aluminium content.

It is of interest to know whether the soil goethite from one soil is uniform in composition or whether the goethite is variable, the above

[1] A fine-grained diaspore suffered less than 1 per cent. loss when subjected to the dithionite treatment.

data being an average for the whole material. Physical separates (different particle size fractions) and chemical separates (successive dithionite extractions) were therefore analysed to determine the uniformity of the goethites.

Table 4 shows the experimental data from the analyses of successive dithionite extractions of different particle size fractions of BS 29 (NaOH treated). Table 5 shows the mineralogical composition of the residues from the dithionite treatments. Quartz is the main mineral of the residues, and, not surprisingly, the amount of residue increases with

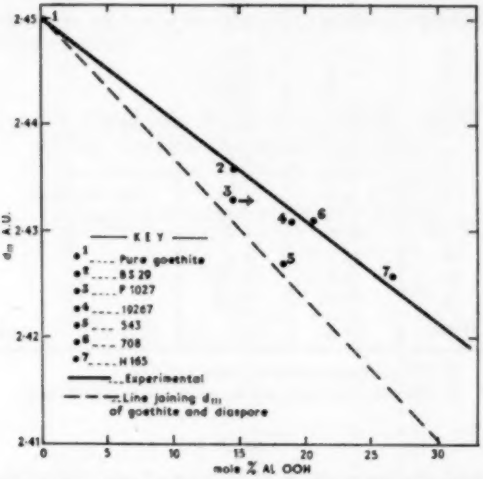

FIG. 1. Relationship between d_{111} and Al content of soil goethites.

increasing particle size. Some goethite remains even after three dithionite treatments in the finest particle size.[1]

The compositions of the goethites for each particle size of BS 29 have been calculated in Table 6 from the total iron and aluminium extracted by the successive dithionite treatments. The aluminium content of the goethite decreases with increasing particle size and the d_{111} spacing shows an accompanying change.

The variation in FeOOH:AlOOH ratio with successive dithionite treatments is shown in Table 7. The iron and aluminium extracted by the first treatment gives much the same ratio for the different particle sizes. For each particle size the second and third extractions give ratios which are in good agreement with each other but less than the ratio for the first extraction. The ratio given by the second and third extractions show a marked increase with increasing particle size. The ratio for the third extraction of the 5–20 μ fraction is very low due to the fact that a

[1] G. Turton (priv. comm.) of this Division found that only about half the goethite in the clay ($< 2\,\mu$) of BS 29 was removed by a modification (Haldane, 1956) of the acid oxalate method of Jeffries (1941, 1946).

TABLE 4

Iron and Aluminium Removed by Successive Dithionite Treatments of Different Particle Sizes of Soil Goethite BS 29*

Particle size (microns)	*Dithionite treatment*	Fe_2O_3 %	Al_2O_3 %	*Ignition loss 400° C.*	*Insoluble residue* %	*Total* %
< 0·5	1	45·1	3·0			
	2	13·5	3·0			
	3	5·8	1·3			
	Total	64·4	7·3	..†	12	..
0·5–2	1	43·5	3·4			
	2	11·5	2·3			
	3	3·5	0·61			
	Total	58·5	6·3	13·1	23	100·9
2–5	1	38·7	2·6			
	2	11·4	1·7			
	3	4·3	0·61			
	Total	54·4	4·9	11·5	28·6	99·4
5–20	1	35·4	2·5			
	2	5·8	0·67			
	3	0·07	0·13			
	Total	41·3	3·3	9·9	45·3	99·8

* All analyses done on 100–150 mg.
† Insufficient material to estimate ignition loss.

TABLE 5

Mineralogical Composition of Residues from Three Successive Dithionite Treatments of BS 29 (NaOH *treated*)

Particle size (microns)	*Minerals identified*				
	Quartz	*Anatase*	*Rutile*	*Goethite*	*Clay*
< 0·5	moderate	very little	very little	moderate	possible trace
0·5–2	much	very little	very little	..	possible trace
2–5	much	very little	very little	..	possible trace
5–20	much	very little	very little	..	..

negligible amount of iron was removed, so that even a trace of aluminium from other sources would alter the ratio considerably.

The change in average composition of the goethite after one dithionite extraction is reflected in the X-ray diffraction pattern. The samples BS 29 (0·5–2 μ) and H 165 (< 2 μ) gave peaks at 2·4364 and 2·4260 Å. which shifted to 2·4306 and 2·4201 Å. after the first dithionite extractions.

For reasons given earlier the simple dithionite method (Mackenzie, 1954) was used for removing the free iron oxides in preference to the modification of this method (Aguilera and Jackson, 1953). However, as the dithionite by itself was not very effective in removing even fine-

TABLE 6

Composition of Soil Goethite, BS 29, *as a Function of Particle Size*

*Particle size** (*microns*)	*Molar composition*		*Molar ratio* FeOOH/AlOOH	d_{111} Å.
	FeOOH	AlOOH		
< 0·5	0·849	0·151	5·6	2·433
0·5–2	0·855	0·145	5·9	2·436
2–5	0·863	0·137	7·1	2·436
5–20	0·888	0·112	8·0	2·444

* The coarser fractions are mixtures which contain much fine material in addition to the coarse material—see text.

TABLE 7

Ratio of Iron to Aluminium in Successive Dithionite Extractions of Soil Goethite BS 29 (*after* NaOH)

Particle size (*microns*)	*Dithionite treatment*	$\frac{\text{FeOOH}}{\text{AlOOH}}$
< 0·5	1	9·6
	2	2·9
	3	2·85
0·5–2	1	8·2
	2	3·2
	3	3·6
2–5	1	9·5
	2	4·3
	3	4·5
5–20	1	9·1
	2	5·5
	3	(0·3)

TABLE 8

Iron and Aluminium Removed from BS 29 (0·5–2 μ, NaOH) *by Dithionite-Citrate System Buffered with Sodium Bicarbonate* (*Mehra and Jackson, 1960*)

Extraction	Fe_2O_3	Al_2O_3	*Molar composition*	
			FeOOH	AlOOH
1	61·2	6·5	..	..
2	0·3	not detected	..	..
Total	61·5	6·5	0·864	0·136

grained (0·5 μ) aluminous goethite it was decided to try one of the recent methods (Mehra and Jackson, 1960) based on dithionite. The results of this extraction on a fraction of BS 29 are given in Table 8. It is seen that complete removal of the goethite was accomplished in one treatment, the total iron and aluminium removed agreeing with that removed in three simple dithionite treatments (Table 4). The effectiveness of

this method is probably due, as suggested by Mehra and Jackson, to the increased reducing power of the dithionite at pH 7·5, but the use of citrate may be an important factor in dissolving *aluminous* goethites as it has been shown that citrate can remove aluminium from soil (Saunders, 1959).

D.T.A. analyses were made of a number of particle sizes of the soil goethites since the presence of aluminium in goethite might change its thermal behaviour. However, all the endothermic reactions occurred in the normal range (300°–370° C.) and there were no systematic variations in peak temperature which could be attributed to aluminium content. If the presence of aluminium in goethite alters its thermal behaviour, then the change is small compared to the variations, due to particle size and other causes, found in natural goethites. The D.T.A. diagrams are not shown but some (Ferrite yellow, $< 2\ \mu$; H 165 $< 2\ \mu$) endotherms exhibited the doubling discussed by Kelly (1956).

Discussion

The above chemical and X-ray data show that aluminium can replace iron in goethite to at least 25 mol. per cent., a conclusion which is in agreement with the observations of Correns and Engelhardt (1941) who found aluminium contents up to 15·9 mol. per cent. in their oolitic goethites. Careful measurements of the X-ray diffraction spacings of goethites in many other soils showed that most soil goethites ($< 2\mu$ fraction) have a lower spacing than that of pure goethite, indicating aluminium to be a common replacement for iron. In fact it is difficult to obtain a soil goethite ($< 2\ \mu$) which has normal diffraction spacings. This fact accords well with the observation that, almost invariably, reasonable amounts of aluminium are extracted from soils in the process of removing free iron oxides, the relative amounts of aluminium and iron often being comparable to those shown in Table 3 (Williams *et al.*, 1958; Williams, 1950; Mackenzie, 1954). The removal of aluminium with the iron is so common that it has led certain workers to refer incorrectly to these treatments, which are specifically designed for the removal of iron, as methods for removing sesquioxides. The aluminium removed by these treatments is generally considered to come from attack on clay minerals, or crystalline or amorphous aluminium oxides. Undoubtedly these are all sources of aluminium but the present work shows that most of the goethites themselves are to be regarded as a source of aluminium. Comparisons of the dithionite method with the more acid free iron removal treatments show that in the acid solution much more aluminium is removed, presumably from clay minerals or aluminium oxides (Williams *et al.*, 1958; Mitchell and Mackenzie, 1953; Mackenzie, 1954).

The difficulty in removing goethite using the simple dithionite treatment seems to be associated with the presence of aluminium in the goethite lattice. In the present study the ease of removal of iron from different particle sizes of the one clay was inversely proportional to the amount of aluminium present (Table 4) and it led to the surprising

result that goethite was removed more easily from the 5–20 μ fraction (complete with two treatments) than from the $< 0{\cdot}5$ μ fraction (incomplete after three treatments). In this laboratory it has been noted that hematite is generally more easily removed from clays than goethite, and this experience agrees with that of Mehra and Jackson (1960). However, Schwertmann (1959) states that the removal of hematite proceeded more slowly than goethite. He does not indicate the particle size to which this observation applied but some of the samples he was using were coarse grained, and it is possible that these goethites, which are probably low in aluminium, are more soluble than hematite in dithionite.

It should be particularly noted that the loss of colour is an unreliable method of determining when all the goethite has been removed from a clay. After one or two dithionite treatments many of the clays studied assumed a pale cream colour which suggested the complete removal of goethite. X-ray diffraction patterns of these clays indicated that goethite was still one of the dominant minerals. If a small amount of hematite is present to render the clay red or brown, a dramatic colour change can often be achieved with one dithionite treatment, but this is no proof of the complete removal of goethite. The most difficult goethite to remove (Table 7) is that highest in aluminium, and it is possible that this goethite, which is at least 25 mol. per cent. aluminium, has a paler colour than pure goethite.

The analyses of the different particle sizes of BS 29 show the smallest particle sizes to be highest in aluminium. This is not surprising as the stresses produced in replacing iron could limit the size to which crystals grow. Of the clay goethites studied, H 165 has both the highest aluminium content and the smallest average particle size—about 0·02 μ, from surface area and electron micrograph measurements. Apparently only the relatively pure goethite crystals can grow to appreciable sizes under normal conditions so that coarser fractions from the soil contain less aluminium. Measurements on the coarser iron oxide fractions used in this study indicated that their average particle size was very much smaller than their nominal values. Studies of electron micrographs show that the coarser fractions contain some very fine material. It is probable that when the particle size separations were made much of the fine goethite remained in aggregates with itself or with clay. If the particle size separations were more specific, i.e. if the coarser fractions were not mixtures, the phenomena varying with particle size (aluminium content, solubility in dithionite, cell dimensions) would undoubtedly show more dramatic changes.

Although Correns and Engelhardt (1941) observed aluminium in macroscopic crystals of goethite these appear to be rare as an examination of many mineral goethites of different origins failed to reveal any coarsely crystalline samples containing appreciable aluminium.

The reduction in unit cell size observed by Correns and Engelhardt is to be expected since the Al^{3+} ion has a smaller radius (0·57 Å.) than the Fe^{3+} ion (0·67 Å.). No accurate relationship between aluminium content and unit cell dimensions is obtainable from their data. Although all the axes are decreased with increasing aluminium content *a* and *b*

show the biggest reduction. The experimental data given in Fig. 1 show that the (111) spacing decreases with increasing aluminium content. Sample P 1027 contains hematite (Table 2), and correction for this would displace its point towards the experimental line. Why sample A 543 lies so far below the experimental line is not known, but this sample is comparatively low in goethite—only 25 per cent. after NaOH attack—and the presence of a small amount of any other mineral which could yield iron in the dithionite treatment could cause the discrepancy. The broken line of Fig. 1 is that joining the (111) spacings of goethite and diaspore. The experimental line deviates significantly from this, probably due to the fact that the three axes of the unit cell do not all contract at the same rate. The (111) spacing is most sensitive to changes in the *c* axis, this being the smallest. Assuming that the incorporation of aluminium in the lattice involves a certain volume decrease, the data suggest that the decrease is accomplished primarily by contraction of the *a* and *b* axes. Attempts to calculate unit cell dimensions directly from the powder diffraction data were unsuccessful as only comparatively few lines could be measured accurately, the high angle lines being too broad.

Soil goethites commonly give broad diffraction lines but some caution would need to be exercised in applying the formula relating particle size and line broadening to determine particle sizes. The data of Tables 6 and 7 suggest that soil goethite is not a uniform material so at least some of the line broadening could be due to the superposition of slightly different patterns. Particle sizes calculated under these conditions would be too small.

That soil goethites contain appreciable amounts of aluminium is not surprising as most other forms of iron oxide commonly contain aluminium. Apart from Correns and Engelhardt (1941), Beneslavsky (1957) appears to be the only author to demonstrate aluminium as a constituent of goethite. Beneslavsky found about 20 mol. per cent. aluminium in goethites present in bauxite, and these goethites gave X-ray diffraction patterns with reduced spacings. Hansen and Brownmiller (1928) have synthesized hematite containing appreciable amounts of aluminium and Beneslavsky (1957) observed similar hematites in bauxite. Magnetite commonly contains aluminium (Palache *et al.*, 1944).

Attempts to synthesize goethite containing aluminium were only partially successful. Goethites with diffraction spacings lower than normal were obtained by crystallization of the hydrolysis product of a ferric sulphate solution in the presence of aluminium hydroxide. However, the results were not very reproducible and the final products were not pure enough for analysis.

The recognition of goethite as an aluminium-bearing mineral in soils could be very important in understanding the phosphate fixing powers of this mineral as the presence of 20–30 mol. per cent. of aluminium may alter this property considerably. Williams *et al.* (1958) have established correlations between the phosphate sorption capacity of soils and the aluminium removed by various extractants, particularly dithionite and Tamm's acid oxalate solution. The interpretation of data such

as this will be aided by the recognition of goethite as a source of aluminium.

It is probable that the amount of aluminium present in goethite is related to weathering conditions and therefore to soil type. More samples are being studied to see if such a relationship exists.

Conclusions

Soil goethites were extracted, almost pure in some cases, from kaolinitic soil clays by boiling the clays in NaOH solution.

The soil goethites studied in detail contained between 15 and 30 mol. per cent. aluminium replacing iron. The presence of aluminium reduces the unit cell size so that the powder diffraction spacings have lower than normal *d* values.

Most soil goethites would seem to contain appreciable amounts of aluminium since almost invariably their diffraction lines are displaced in a direction indicating a smaller cell size.

The presence of aluminium in the goethite accounts for much of the aluminium brought into solution by treatments designed to remove iron oxides only. Using the simple dithionite method for removing iron oxide the ease of removal is inversely related to the amount of aluminium in the goethite, so that in some cases fine goethite ($< 0{\cdot}5\ \mu$) is not removed by three treatments. However, some of the more recent modifications of the dithionite treatment appear to be effective even for these goethites.

The goethite of smallest particle size contains the most aluminium and it is probably the presence of foreign ions which restricts crystal growth.

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THE ADSORPTION OF CATIONS FROM SOLUTION BY ALLOPHANE IN RELATION TO THEIR EFFECTIVE SIZE

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Summary

The amounts of cation physically adsorbed from neutral-salt solutions by allophane and co-precipitated silica-alumina mixtures are dependent upon the effective radius of the cation. For non-hydrated cations, the B.E.T. theory indicates that about the same area of surface is covered by a monolayer of cations, the sizes of which may vary considerably. The results for hydrated cations are consistent with the idea of effective size as a factor in the mechanism of adsorption if the hydration numbers of Glueckauf are regarded as relevant to the process. When using leaching methods which allow the retention of most of the physically adsorbed cation (as is the case when alcohols are used to remove excess salt), cation-exchange-capacity values are in inverse order to the effective radii of the cations. This will apply to silica-alumina catalysts as well as to soils containing allophane.

Introduction

It has been pointed out by the writer (Birrell and Gradwell, 1956) that allophane separated from New Zealand volcanic-ash soils, and other amorphous soil constituents of the hydrous sesquioxide type, adsorb cations from salt solutions in a manner which strongly resembles the physical adsorption of gases on solid surfaces. In fact, by making the appropriate substitution of concentration terms for the pressure terms used in gas adsorption studies, good agreement with the well-known Brunauer-Emmett-Teller (B.E.T.) theory can be demonstrated for the uptake of cations from solution by these materials. A necessary condition is, however, that the pH of the system should remain fairly constant over the range of salt concentrations used. This condition was found to be met when acid-washed samples of allophane were brought to equilibrium with neutral acetate solutions. Wada and Ataka (1958) have also demonstrated that the ammonium cation appears to be physically adsorbed from solutions of ammonium chloride by allophane-containing fractions separated from Japanese volcanic-ash soils.

It therefore seemed worthwhile to carry out equilibrium experiments with allophane-rich soil fractions and a suitable series of neutral acetate solutions, using cations covering a range of effective sizes in solution. By applying the B.E.T. theory to the results, and using available values for the cross-sectional areas of the cations, it would be expected that, if the physical adsorption concept is correct, concordant values would be obtained for the amount of surface of the adsorbent which is covered by a monolayer of cation.

It was observed also that when natural allophane soils or their acid-washed clay fractions were leached with these neutral acetate solutions, the pH of the leachates did not fall much below the original value of

7·0. It has also been shown (Birrell and Gradwell, 1956; Wada and Ataka, 1958) that subsequent washing of the material with 80 per cent. ethyl alcohol removes only a small part of the physically adsorbed cation. By adjusting the concentration of the leaching solution so that the concentration of cation was always about the same fraction of its saturation concentration, and by keeping the ratio between the volume of alcohol and the weight of sample constant, it would be expected that the C.E.C. values would decrease as the effective size of cation increased.

In addition to testing soil fractions containing allophane by these two procedures, it seemed desirable to compare also the behaviour of (*a*) mixtures of silica and alumina formed by co-precipitation, and (*b*) a bentonite of high C.E.C. value.

Experimental

(*a*) *Preparation of adsorbents*

The Tirau ash subsoil described previously (Birrell and Gradwell, 1956) was treated with hot dilute hydrogen peroxide solution, washed with water, and N sodium hydroxide was added to the aqueous suspension until it was judged that maximum dispersion was obtained. After separating the fraction of the required size by sedimentation, flocculation was effected with sodium chloride. The settled material was washed repeatedly with N/50 HCl, then with 80 per cent. ethyl alcohol, and finally with acetone, before drying at about 35° C. By proceeding in this way, it was found practicable to reduce the sodium content of the product to a value of 0·015 m.e. per g. without serious attack on the allophane.

The co-precipitated mixtures of silica and alumina were made by the procedure of Walling (1950). Before use, the dried products were ground to pass a 100-mesh B.S. sieve and heated to 500° C. overnight. This heating served to drive off exchangeable and adsorbed ammonia introduced during the alumina precipitation. Two preparations were made, one containing 5 per cent. alumina, the other 18 per cent.

The bentonite was a commercial sample from Wyoming, U.S.A., and was mainly of the sodium form as indicated by its liquid limit value (Dr. R. D. Northey, Soil Bureau, pers. comm.).

(*b*) *Methods*

Equilibrium tests were made with acetate or sulphate solutions at 20° C. as described previously (Birrell and Gradwell, 1956). For the allophane fractions, amount of sample, volume, and concentration of solution were chosen so as to give an isotherm up to a reduced concentration value of about 0·4 (reduced concentration = equilibrium concentration of cation/saturation concentration). For the bentonite, which showed negligible change in the amount of cation taken up with concentration of the solution, and for the silica-alumina of 5 per cent. alumina content where this concentration effect was less marked than with allophane, single measurements with monovalent cations were made.

For cation exchange capacity measurements by the leaching method, acetate solutions adjusted to pH 7 were used. For each 2 g. of sample, the volume of leaching solutions was at least 50 ml., and exactly 100 ml. of 80 per cent. w/w ethyl alcohol was used to remove excess salt. The retained cation was determined on N acetic acid extracts of the soils, except in the case of ammonium, where the distillation method was used.

Caesium and rubidium acetates were made from A.R. grade chlorides. Reagent grade lithium and lanthanum acetates were used. Ammonium acetate solution was prepared as described by Metson (1956). Tetra-alkyl ammonium acetate solutions were made from the commercial 25 per cent. w/v solutions of the hydroxides.

Caesium, rubidium, and the tetra-alkyl ammonium cations were determined gravimetrically in their acetate solutions as the chloroplatinates. When rubidium was present as the sulphate, it was estimated by the sodium tetraphenyl-boron method of Cluley (1955).

The purity of the caesium, rubidium, and tetra-alkyl ammonium acetate salts was checked by determining the platinum content of the precipitated chloroplatinates. The calculated equivalent weights differed by less than 1·5 per cent. from the theoretical values.

Lithium and barium were determined as sulphates. Lanthanum was determined as oxalate by the procedure of Kolthoff and Elmquist (1931).

Required solubility values at 20° were determined on a weight/volume of solution basis, values found being:

	m.e. per ml.
Caesium acetate	7·04
Rubidium acetate	6·7
Rubidium sulphate	3·29
Lanthanum acetate	1·575
Tetra-methyl ammonium acetate	6·1
Tetra-ethyl ammonium acetate	3·4

In order to obtain the solubilities of the normal tetra-alkyl ammonium acetates, it was found necessary to evaporate solutions of concentration less than 2 m.e. per ml. after adjusting to pH 7, otherwise the crystals separating were liable to contain excess acetic acid, and lower solubility values resulted. The solubility of ammonium acetate was estimated from data given by Seidell (1940) as 9·5 m.e. per ml.

The effective cross-sections of the cations in solution were taken as $\pi \times (\text{effective radius})^2$. For caesium and rubidium which are not hydrated (Glueckauf, 1955), the radii values given by Pauling (1948) were used. For the tetra-alkyl ammonium cations, which are not likely to be hydrated also on account of their large size, the effective cross-section was calculated from the crystal specific gravities of their halides, taking the radii of Cl^- and Br^- as 1·81 and 1·95 Å. respectively (Pauling, 1948). The value thus obtained for tetra-methyl ammonium agrees fairly well with that calculated from a molecular model by Barrer and McLeod (1955), but the radius of the tetra-ethyl ammonium ion given by the crystal data is about 10 per cent. less than the value from the

molecular model. For the other cations used, which are known to be hydrated, namely, ammonium, barium, lanthanum, and lithium, there does not appear to be any reliable method of calculating the absolute effective radii in solutions (Glueckauf, 1955), and those values which have been found in the literature do not appear to be self-consistent. However, the mean hydration numbers (h values) used by Glueckauf (loc. cit.) to calculate osmotic and activity coefficients seem to offer a useful approach towards arriving at relative effective radii, when combined with the Pauling radii. Accordingly, effective radii (in Å.) have been calculated for the hydrated cations by the formula $\sqrt[3]{\frac{3}{4\pi}\left\{\frac{4\pi}{3}r_+^3+30h\right\}}$, where r_+ (in Å.) is the Pauling radius, and h is the hydration number as given by Glueckauf. The factor 30 relates to the volume of the water molecule, stated by Bernal and Fowler (1933) as 30 Å^3. The values given by this formula are shown bracketed in Table 1, although their actual physical significance is uncertain.

TABLE 1

Surface Coverage of Tirau Ash Fractions by Cation Monolayers

Size of fraction	*pH range of system*	*Cation*	*Effective radius (Å)*	*Correction for non-physical adsorption mg.-at./g.*	*Corrected monolayer value mg.-at./g.*	*Surface covered m.²/g.*
Clay plus silt	5·8–6·8	Cs	1·66	0·08	0·55	29
<20μ. Surface	5·7–6·2	Li	(2·92)	Nil	0·24	..
by gas adsorp-	5·7–6·2	$N(CH_3)_4$	3·02	0·08	0·18	30
tion 160 m.²/g.	6·2–7·2	$N(C_2H_5)_4$	3·66	Nil	0·13	33
Clay < 2μ.	5·3–5·7	Rb	1·49	0·15	0·90	38
Surface by gas	6·0–6·2	Ba	(2·88)	0·12	0·37	..
adsorption	5·4–5·6	La	(3·81)	0·05	0·16	..
230 m.²/g.						

Discussion of Results

(*a*) *Equilibrium experiments*

It has been assumed in calculating the uptake of cation from these that no water is taken up by the adsorbent from the solutions. The justification for this assumption is the agreement with the B.E.T. theory previously obtained over a fairly wide range of concentration (Birrell and Gradwell, 1956). A similar assumption was also made by Wada and Ataka (1958).

Fig. 1 (*a*) shows the uptake of cations by the clay plus silt fraction of Tirau ash subsoil at 20° C., and Fig. 1 (*b*) the results for the clay fraction at the same temperature. The isolated values for different cations with silica-alumina and with the bentonite are shown in Fig. 1 (*c*). Table 1 shows effective radii values for the cations, obtained as mentioned in the previous section, and B.E.T. monolayer surface coverage values calculated from them for the two soil fractions.

Fig. 1 (*a*) shows that the order of cation uptake for the non-hydrated cations is in accordance with their effective radii values, and the lower value of lithium relative to caesium agrees with the moderately high hydration number for the former cation.

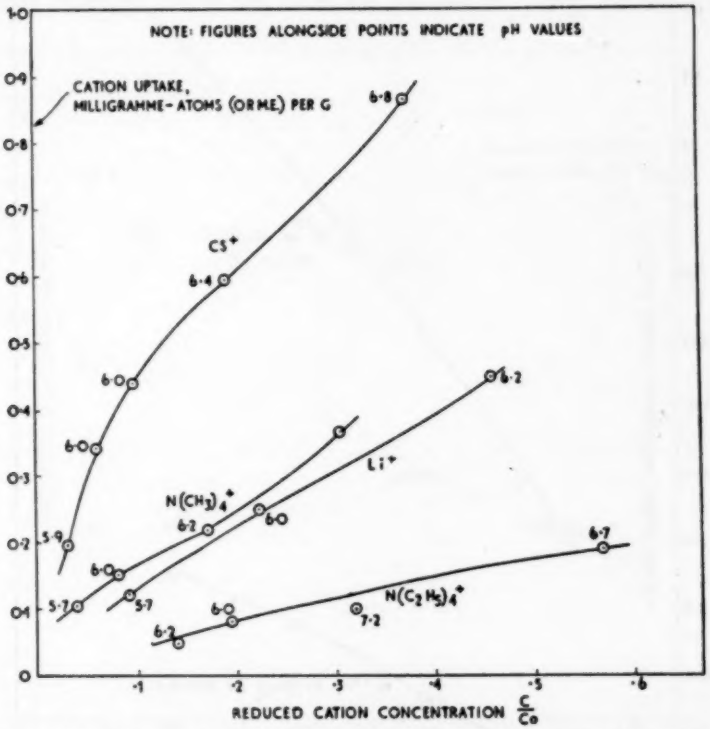

FIG. 1 (*a*). Cation uptake from neutral acetate solutions by clay plus silt fraction (less than 20μ) of Tirau ash subsoil.

In a similar way the orders of uptake shown by rubidium, barium, and lanthanum (the Pauling radii of which do not differ greatly), are consistent with the hydration number values, as explained in the previous section, bearing in mind that physical adsorptions of cations must be compared on a gramme-atom basis.

Certain difficulties arose in the calculation of monolayer values from the adsorption curves, using the B.E.T. theory. These were:

(*a*) Non-physical uptake of cations.
(*b*) Variations in average pH values of the system with different salts.
(*c*) Non-linearity of the plots of $C/(C_0-C)_{x/m}$ against C/C_0. (For notation see ref. 1.)

(*a*) is revealed by the adsorption curves failing to pass through the

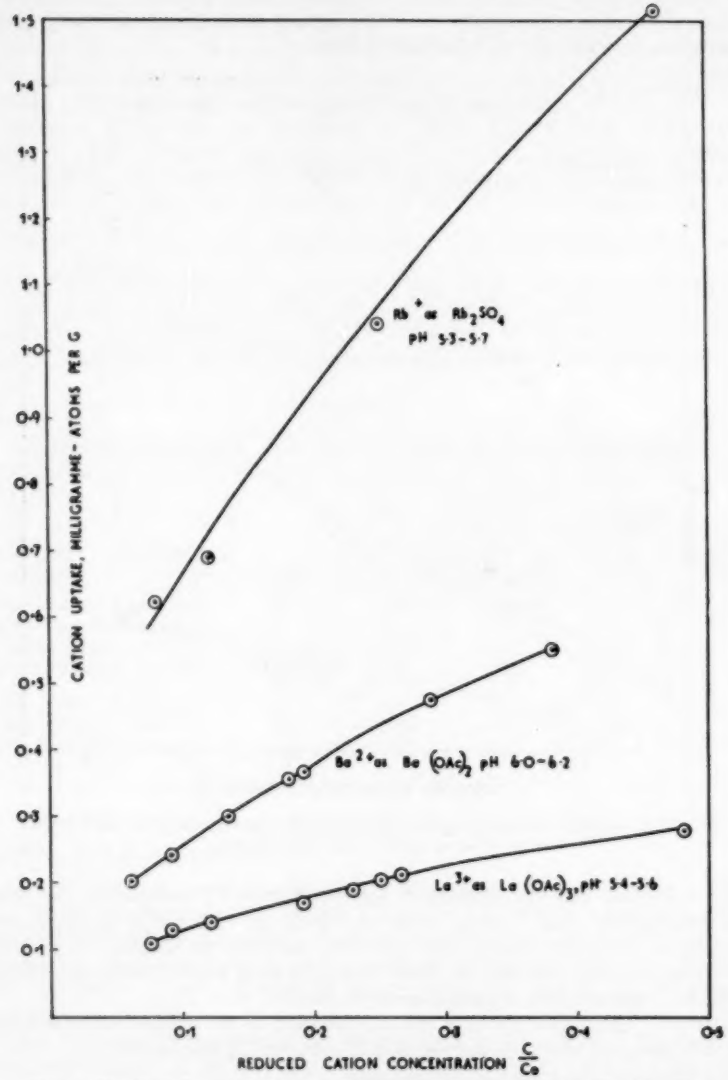

FIG. 1 (*b*). Cation uptake from neutral solutions by clay fraction (less than 2 μ) of Tirau ash subsoil.

origin when extrapolated back to zero C/C_0 value. This effect is due to the exchangeable base content of the soil fractions, and the fact that allophane shows a pH-dependent negative charge (Wada and Ataka, 1958).

The intercept could not, however, be always clearly defined. For

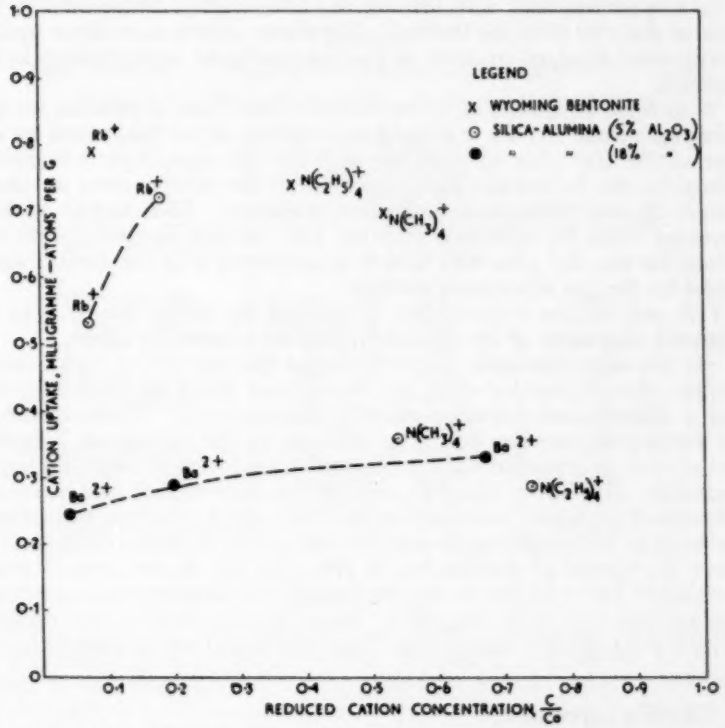

FIG. 1 (*c*). Cation uptake from neutral acetate solutions by bentonite and silica-alumina.

the clay plus silt fraction, caesium and tetra-methyl ammonium indicated about 0·08 mg.-atoms per g. due to this cause, but lithium and tetra-ethyl ammonium did not intersect at positive values of x/m. For the clay fraction, lanthanum and barium gave reasonably definite intercepts. In this case it seemed reasonable to assign 0·15 mg.-atoms per g. as the uptake of rubidium due to this cause. This figure was arrived at by taking three times the lanthanum intercept, since the non-physical adsorption will be on an equivalent basis.

These corrections were applied to the adsorption curves before calculating the monolayer values. In the case of lithium and tetra-ethyl ammonium no correction was made.

(*b*) could not be overcome without tedious adjustment of the pH value of the solutions. Small variations in average pH should be taken care of by corresponding changes in non-physical adsorption values, because the effect of increasing pH is to increase the amount of cation taken up, and vice versa (Birrell and Gradwell, 1956; Wada and Ataka, 1958).

(*c*) was serious only with lithium and tetra-methyl ammonium in the case of the clay plus silt fraction. For these cations monolayer uptake values were assumed to occur at the same reduced concentration as for caesium.

With these adjustments, it can be seen from Table 1 that the surface coverage values for the non-hydrated cations agree fairly well in the case of the clay plus silt fraction, and that the monolayer adsorption values for the hydrated cations conform to the relative sizes as established by the Glueckauf hydration numbers. The higher surface coverage value for rubidium with the clay fraction compared with the values for the clay plus silt fraction is consistent with the surface areas found by the gas adsorption method.

Part only of the total surface is covered by cation, but it is to be expected that some of the remainder will be covered by anion.

For the silica-aluminas, Fig. 1 (*c*) shows that the size of cation has a similar, though smaller effect on the amount taken up from solution, and a distinct concentration effect is also apparent. These materials are extensively used as crackling catalysts in the petroleum industry, and several investigators have published values for their cation exchange capacities. It follows, therefore, that such values will include indefinite amounts of physically adsorbed cation if they are determined by leaching methods in which the excess salt is removed by alcohol washing. The curve for uptake of barium ion at pH 6 by the 18 per cent. alumina material in Fig. 1 (*c*) shows that the non-physical adsorption is relatively greater than it is with allophane. For bentonite, where ionic replacement is the principal mechanism, ionic size makes no significant difference.

(*b*) *Leaching experiments*

The effect of the size of cation on the amount retained by the soil fractions and the silica-aluminas is shown clearly by the results given in Table 2. The only point of doubt is the size of the ammonium ion relative to rubidium. The formula given earlier would indicate that the ammonium ion in solution is larger than rubidium, but smaller than tetra-methyl ammonium which would fit in with the results in the table. Differences would have been greater if the reduced concentrations of the tetra-alkyl ammonium cations had been of the same order as those of rubidium and ammonium, instead of somewhat greater.

The differences shown by the silica-aluminas are rather less than for the soil fractions containing allophane, which is consistent with the rather greater amount of non-physical adsorption shown by the former materials, as mentioned in the previous section. With the bentonite, on the other hand, the large lanthanum ion gives a value close to the

accepted value obtained for this material using smaller cations, even although the excess salt was removed by washing with water. This procedure was found to be necessary on account of the low solubility of lanthanum acetate in alcohol. On the other hand, water-washing of the rubidium-saturated clay plus silt fraction of the Tirau soil reduced the C.E.C. value in this case to 0·14 m.e. per g.

TABLE 2

Cation Exchange Capacities by Leaching with Solutions of Neutral Acetates followed by Washing with 80 per cent. Alcohol

Material	*Cation*	*Reduced concentration of cation in leaching solution*	*C.E.C. m.e./g.*
Tirau clay, $< 2\mu$	Rb	0·13	1·06
	NH_4	0·105	0·44
Tirau clay plus silt, $< 20\mu$	NH_4	0·105	0·35
	$N(CH_3)_4$	0·25	0·12
	$N(C_3H_5)_4$	0·32	0·095
Silica-alumina (18% Al_2O_3)	Rb	0·13	1·08
	NH_4	0·105	0·94
	$N(C_3H_5)_4$	0·32	0·47
Silica-alumina (5% Al_2O_3)	Rb	0·13	0·73
	$N(CH_3)_4$	0·25	0·53
	$N(C_3H_5)_4$	0·32	0·44
Wyoming bentonite	La	0·63	0·82

Conclusions

The amount of physically adsorbed cation taken up by allophane is dependent on the effective size of the cation in solution, as well as upon its concentration. This strengthens the analogy with the observed phenomena of physical adsorption of gases, and the B.E.T. theory may be applied to calculate the amount of surface covered by physically adsorbed salts provided the effective sizes of the ions are known. C.E.C. values for soils containing allophane when determined by conventional leaching methods, will depend upon the effective size of the cation used as well as upon concentration of the leaching solution and the strength and volume of washing alcohol. The same factors will affect the C.E.C. values of silica-alumina catalysts if they are determined in this way.

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MEASURING THE STATE OF REDUCTION OF A WATERLOGGED SOIL

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Summary

E_h and pH measurements and the term $r_{E_h} = E_h + 3 \times 2{\cdot}3\, RT/F$ pH have been tested under simulated field conditions and errors assigned to them. The author considers that, whilst E_h measurements in the field may be used to differentiate between reduced and oxidized soils, their error is too large for them to supply more precise information about the state of reduction of a waterlogged soil; he also considers that there is little point in adjusting these measurements for pH change.

It is proposed that an estimation of the concentrations of the two states of iron in a waterlogged soil should be used as the basis of a field method for measuring the soil's state of reduction.

The results give some support for the argument that the equation

$$E_h = K - k \log c_{Fe^{++}} - 3 \times 2{\cdot}3 \frac{RT}{F} \text{ pH}$$

is applicable to waterlogged soils.

In previous papers (Jeffery, 1960, 1961) the author has given evidence that the equation

$$E_h = 1{\cdot}033 - 0{\cdot}0601 \log c_{Fe^{++}} - 0{\cdot}180 \text{ pH (at } 30°) \qquad (1)$$

probably holds for waterlogged soils, providing solid $Fe(OH)_3$ is present. Assuming it to be correct he applied it to define the state of reduction of any given paddy soil and showed how this may be related to optimum fertility conditions.

In the exhaustive introduction to his work Ponnamperuma (1955) derived a similar equation but brought no evidence to support it and in presenting his results he employed $\Delta E_h/\Delta \text{pH} = -80$ mV. His values for E_h, pH, and c_{Fe} do not support equation (1) at all well although they do support the present author's hypothesis in the following ways: (*a*) they show that a gradual increase in ferrous iron occurs in a healthy paddy soil over a considerable period of time—as opposed to a rapid increase within the first few days of submergence, (*b*) the results for c_{Fe} in the soil percolates are of the order of 1×10^{-3} mg. e./l., (*c*) the plots of E_h/time and pH/time (p. 164) tend to suggest $\Delta E_h/\Delta \text{pH} = -180$ mV.

In order to test (1) further and to examine the validity and practicability of using it in the field, two soils of widely differing iron contents were placed in series of buckets and maintained under various constant water conditions from 30 per cent. field capacity to completely submerged. Rice was grown in one group of buckets and the other was kept bare. The pH, E_h, and c_{Fe} values of the soils were recorded at intervals.

The results are used to suggest the basis for possible routine methods for measuring the state of reduction of a given soil.

Experimental

Soils

	Organic content	Fe *content*	*Water-holding capacity*
Rokupr 1 . .	3·5 g. C/100 g.	3·6 g. Fe/100 g.	46%
Kontobi 5 . .	1·9 g. C/100 g.	0·4 g. Fe/100 g.	16%

Buckets

Twenty-one-pound samples of the soils were maintained under the following water conditions in 2½-gallon polythene buckets: 30%, 50%, 70%, 95%, 100%*a*, 100%*b*, 100%*c*, 1 in. standing water, 6 in. standing water, where the percentages refer to field capacity and *a* = no additional treatment, *b* = soil allowed to dry to 95% and then restored to 100%, and so on, and, *c* = with limited free drainage. Each treatment was set up in triplicate. The buckets were weighed each morning and tap water added to make up evaporation losses.

After one month 6-week-old rice plants (Tai Chu 65) were planted in two buckets of each triplicate, the third being maintained bare. An initial run was also performed, using quadruplicates, all planted to rice, on Rokupr 1 soil only.

Extractions

Once a month roughly 30-g. samples of soil were taken from each bucket and immediately inserted in jars containing solutions of N K_2SO_4 + H_2SO_4 such that the final pH was about 1·2 (limits 1·0 to 1·5). The extracts were shaken for 2 hours and then filtered. The method is taken directly from the Bremner and Shaw (1955) method for soil nitrogen and the filtrates will be referred to as the BS extracts.

E_h, pH, *and* c_{Fe}

E_h and pH determinations were made on the soil in the buckets and on the BS extracts using the saturated calomel electrode against bright platinum and glass electrodes. c_{Fe} in the BS extracts was determined by dipyridyl (Piper, 1950).

Dichromate titrations

Ten-ml. aliquots of the BS extracts, their pH adjusted to 0·5 with H_2SO_4, were titrated with 0·1 N dichromate and the course of the titration followed potentiometrically.

Results

The Bremner and Shaw extracts

From $E_0 = \Delta - 0{\cdot}06$ pH (Britton, 1955, p. 86) and equation (1), $c_{Fe^{++}}$ should be about 10^{-5} molar for a solution of ferrous ions in contact with the air at pH 1. Sidgwick (1952, p. 1334), citing Ennos (1913), gives 0·03 per cent. 0·1 N Fe^{II} oxidized per hour for, presumably, a neutral solution. An initial check on the BS extracts showed no oxidation of added Fe^{II} over 2 days and, therefore, the extracts were considered suitable for examining the concentrations of the two states of

iron in the soil since, whilst any ferrous iron present would probably be safe from oxidation, large quantities of comparatively inert ferric iron would probably not be removed. For comparisons of the various fractions of iron removed by various methods see Robichet (1957).

Ten-ml. aliquots of these extracts were titrated against 0·1 N dichromate at pH 0·5 and typical results are shown in Fig. 1.

The curves show only one inflexion and from comparing them with that for a 10-ml. aliquot of 0·01 N Fe^{II} in a BS solution it would appear that its position is due to the Fe^{II} content of the extracts. This was verified by assuming that the point of inflexion was due to the Fe^{II} and comparing the values thus found with those obtained by colourimetry; in nearly all cases good agreement was found. Table 1 illustrates the results.

TABLE 1

mg.e. of Ferrous Iron per Litre in the BS Extracts after 81 Days Growth

		Bucket water treatments								
Soil	*Method*	30%	50%	70%	95%	100% *a*	100% *b*	100% *c*	1″	6″
Rokupr 1	dipyridyl	3·4	3·1	0·8	0·9	26·5	6·1	24·2	28·6	28·7
	dichromate	0·5	—	1·0	1·5	24·0	7·5	24·0	—	32·0
Kontobi 5	dipyridyl	0·6	0·6	0·8	0·7	0·9	—	0·9	1·3	—
	dichromate	0·4	—	0·4	—	0·8	1·2	0·8	1·4	1·4

Measuring the E_h of a reduced soil

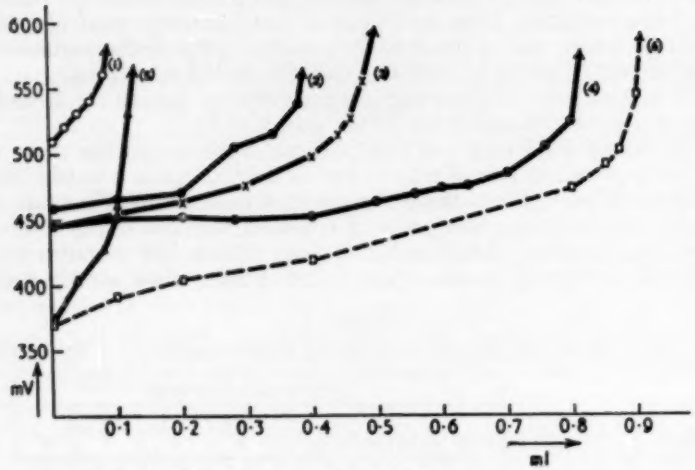
The primary object of this work was to establish the validity of equation (1) when applied to field measurements. Quite apart from the theoretical correctness of the equation, it may well be, for example, that (1) holds for certain localized micro-volumes in a reduced soil but does not hold for the summed effects of these and other micro-volumes which will be measured by the platinum electrode.

Several different methods of measuring soil E_h were tested but, since the BS extracts were so promising, only one was tested at length and will be reported here.

For the drier buckets a small hole, 2 in. deep, was made in the surface of the soil, filled with distilled water, and a platinum electrode inserted. The soil was pressed back tightly around the electrode and the circuit completed through a direct reading potentiometer and saturated calomel electrode. The platinum electrode was then gently agitated in the soil until the potentiometer needle deflected no further (almost invariably in the negative direction) when the agitation was stopped and, after the subsequent rapid movement of the needle had ceased, ignoring gradual drift, a reading was taken; after 2 minutes a second reading was taken. For the wetter buckets the procedure was the same except that no distilled water was added to the hole.

A somewhat similar procedure was adopted for soil pH using the glass electrode.

This was the most direct method tested and it seemed to the author to be of the kind most likely to be serviceable in the field on the large



(1) Rokupr 1, with rice, 30%, 50%, 70%, 95%.
(2) ,, ,, 100% *c*.
(3) ,, ,, 6 in. standing water.
(4) ,, ,, 1 in. standing water.
(5) Kontobi 5, without rice, 6 in. standing water.
(6) BS solution with 10 ml. 0·01 N $FeSO_4$ added.
Kontobi 5 with the 30%, 50%, 70%, and 95% treatments was similar to (1).

FIG. 1. BS solutions titrated with 0·1 N dichromate at pH 0·5.

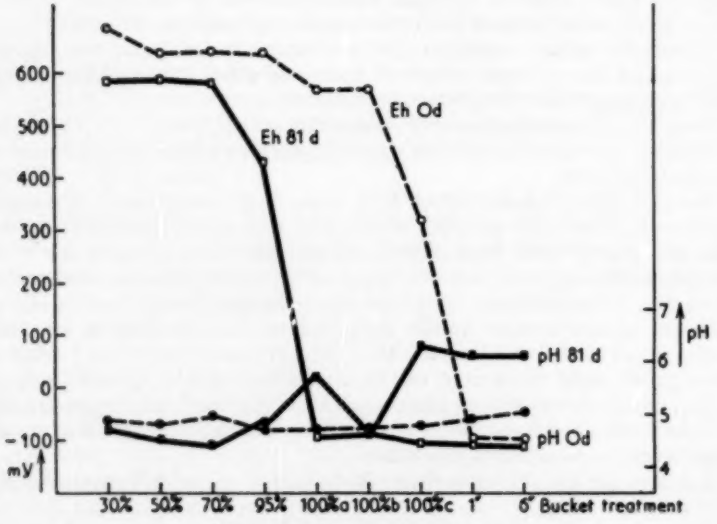


FIG. 2. Rokupr 1 soil, with rice.

scale. It was hoped that the differences between the 2-minute readings would give an estimate of the precision of individual readings and that measurements in replicate buckets would give an estimate of their reproducibility when measuring replicate conditions in the field. Fig. 2 illustrates some of the results for Rokupr 1. The pH of the wetter buckets rose from 5·0 at planting (1 month after the soil was submerged) to about 6·2 at harvest. This supports the results of many workers (see Ponnamperuma, 1955, p. 7 for discussion and review of the literature) and would be expected assuming the gradual and continuous release of Fe^{II} into the soil solution.

TABLE 2

Measurement		*Error d.f.*	*Error variance*	
Drift of individual measurements over 2 min.	wetter soils	59	0·013 v.	(1)
	drier soils	40	0·035 v.	(2)
Replicate soil conditions represented by replicate buckets	wetter soils	23	0·130 v.	(3)
	drier soils	18	0·542 v.	(4)
pH readings on replicate soil conditions	—	35	0·16 pH unit	(5)
r_{E_h} from replicate soil conditions	wetter soils	23	0·17	(6)
r_{E_h} from (1) and (5)	—	—	0·04	(7)

wetter soils = buckets with 100%, 1 and 6 in. moisture conditions.
drier soils = buckets with 30%, 50%, 70%, and 95% moisture conditions.

The E_h of the 100 per cent. buckets has fallen by 81 days to levels comparable with those for the totally submerged samples—including 100% *b* which has been continuously varied between 100 and 95 per cent.

Kontobi 5 soil showed very little change in pH over the whole period —remaining at about 5·5 for the wetter buckets and at about 4·8, or a little higher, for the drier. The E_h curves presented the same overall picture as those for Rokupr 1 but the points were much more erratic.

The wider variations of the E_h readings for Kontobi 5 and the general wide variations in the readings for the 100 per cent. buckets largely contributed to the large errors (3) and (6) in Table 2.

Assuming normal distribution, the standard deviations for the measurements are set out in Table 2. From this table it may be seen that the individual E_h measurements can be made with some precision and that differences of less than 0·05 in the resultant r_{E_h} values should be significant at the 1 per cent. level without the necessity of having recourse to very large numbers of replicate measurements. Table 2 of the author's previous paper (Jeffery, 1961) requires a least significant difference of less than 0·05 for it to be serviceable.

The error for r_{E_h} from replicate buckets, however, is much too large for it to be of use and differences of E_h values of less than 0·1 v. for waterlogged soils and of less than 0·5 v. for aerated soils appear to be of no real significance.

The error for pH was calculated from the quadruplicate measurements made on the initial run since replicate pH measurements were not performed on the second run.

The state of reduction of a waterlogged soil

In Table 3 a small selection of data relevant to the state of reduction of the two soils under varying conditions are collected. The means for '1 inch standing water' with '6 inches standing water' and 70 per cent.

TABLE 3

Soil and its % moisture		*Days from planting*	*mg.e.* Fe^{I} */100 g. soil*	Fe^{II} *as % total extractable iron*	E_h *BS extracts*	E_h *soil*	r_{E_h}
Rokupr drier with rice	70%	0	0·16	1	0·721	0·645	1·54
	95%		0·10	1	0·725	0·645	1·49
	70%	28	0·23	2	0·711	0·631	1·42
	95%		0·38	3	0·715	0·595	1·48
	70%	56	2·7	20	—	0·623	1·52
	95%		1·7	13	—	0·474	1·37
	70%	81	0·32	2	0·705	0·585	1·39
	95%		0·34	3	0·683	0·436	1·29
Rokupr wetter with rice	1″	0	3·7	28	0·653	−0·095	(0·79)
	6″		3·7	28	0·646	−0·091	(0·82)
	1″	28	3·5	27	0·643	0·041	1·11
	6″		2·2	17	0·659	0·101	1·13
	1″	56	10·7	81	—	−0·073	1·09
	6″		6·5	50	—	−0·113	1·11
	1″	81	9·38	71	0·591	−0·097	1·10
	6″		11·65	89	0·611	−0·109	1·01
Kontobi wetter with rice	1″	0	0·21	59	0·629	−0·091	(0·78)
	6″		0·20	57	0·603	−0·101	(0·66)
	1″	28	0·36	100	0·577	0·241	1·18
	6″		0·29	81	0·587	0·141	1·08
	1″	56	0·18	50	—	−0·153	0·98
	6″		0·29	81	—	−0·151	1·00
	1″	81	0·42	119	0·619	−0·079	0·93
	6″		—	—	—	−0·091	0·93

with 90 per cent. are paired since it would appear that the pairs are, for this purpose, identical treatments and they thus give a measure of the reproducibility of the results.

Any columns serve to distinguish the aerated soil from the waterlogged—and may thus be used as the basis for a definition of 'oxidized' and 'reduced' soils—but for the finer distinctions of differences between waterlogged Rokupr 1 and waterlogged Kontobi 5 and between the same soil after different periods of submergence the position is less clear. The E_h figures provide no information and the r_{E_h} values, although arranged in the kind of pattern demanded by the author in his previous paper ((*a*) aerated soil r_{E_h} greater than 1·3, (*b*) values for Kontobi 5 lower than those for Rokupr 1, (*c*) values become lower with time, (*d*) Kontobi 5 figures suggest a state of complete reduction from day 0), all the actual figures for the submerged soils fall into the 'extremely reduced' zone. The four bracketed day 0 figures are, of course, extremely anomalous.

The per cent. Fe^{II} columns, however, do fit very neatly into the

pattern required by equation (1): (*a*) there is very little Fe^{II} extracted from the aerated soil, (*b*) Kontobi 5, a soil very low in extractable iron and therefore to be expected to be reduced right from the very start, has all its extractable iron in the Fe^{II} form at day 0, and (*c*) for the submerged Rokupr 1 soil there is a steady increase in the Fe^{II} extracted with time although the large quantities of readily extractable iron are not entirely in the Fe^{II} form after 81 days (which is after 109 days continuous submergence). Hence a determination of the fraction of the relevant soil iron that is in the ferrous form would appear to be an immediate and very sensitive method of providing information on the state of reduction of a given soil. The figures in the column giving the E_h of the BS extracts suggest the E_h measurements of suitable soil extracts would be a rapid method for obtaining an approximate estimate of this fraction.

The results from the remaining buckets, including those without rice, fitted into the same picture. The results from the initial run also agreed with it although the observations on this run were done in less detail.

Discussion

Table 2 demonstrates conclusively that direct E_h measurements on aerated soils are subject to too much error to have any significance or provide any useful information. This is in accordance with the work of previous workers (see, for example, Heintze, 1934). Less direct methods, however, might be of value (Lamm, 1956). E_h measurements do provide a definition of the difference between oxidized and reduced soils (Pearsall, 1950) but the difference in many cases could be established more easily by inspection.

For reduced soils the error variance for E_h is much lower, however, to establish a difference in soil E_h of less than 50 mV. would require a great many replicates and, when one considers that the pH determinations are also subject to error it seems very doubtful if adjusting field E_h measurements for pH change can have any real significance. This will still be true even allowing that (3) in Table 2 is unduly high because it includes as error some differences that were in fact differences in the oxidation states of the individual buckets (which the figures for some of the 100 per cent. buckets did suggest although there appeared to be no way of objectively allowing for this in the statistical analyses).

The author's r_{E_h} term is subject to the same criticism and, in addition, as illustrated in Table 3, it gives values for all the submerged samples that fall in the 'extremely reduced' range although all the buckets grew healthy rice. This last criticism might be surmounted by arguing that the wrong constant term is being employed in equation (1) and indeed the titrations of the BS extracts tend to indicate an E_0 of about 0·670 for the $Fe^{++} \rightleftharpoons Fe^{+++}$ system, thus making the constant in (1) 0·930 which then gives, at 30°:

	r_{E_h}
Oxidized soil	greater than 1·20
Healthily reduced soil . .	1·20 to 1·10
Extremely reduced soil . .	less than 1·10

This fits the observed results much better and also fits the results of Ponnamperuma.

If the correct constant term can be determined the results would support using r_{E_h} to provide the ultimate definition of the state of reduction of a waterlogged soil but it is very doubtful if it can be usefully employed on field measurements. r_{E_h} has the advantage over the per cent. Fe^{II} expression as an ultimate definition of the state of reduction of a waterlogged soil of being dependent on the ferrous ion concentration in the soil solution and thus it allows for a soil, very high in iron, which although only 50 per cent. reduced as expressed by Fe^{II} has too high a concentration of soluble iron for the healthy growth of rice.

The extraction method seems to offer a very sensitive and simple method of measuring the state of reduction of a waterlogged soil in the field providing that one can be found that will remove all the ferrous iron but only the relevant ferric iron. Alternatively, the relevant ferric iron could be determined by a second method. An extraction method would be particularly useful since it relies on techniques that are already much employed for field work. It would also have the advantage over field E_h measurements that several samples of the same soil can be bulked and also, if samples of reasonable size are taken and immediately thrust into waiting extracting solutions, the problem of oxidation on sampling would be largely overcome. The extracted samples could then be carried back to the laboratory and analysed at leisure (provided they do not change with storage) and this would save a good deal of time in the field. It is difficult to select an entirely suitable extraction method for waterlogged-soil iron, particularly if it is designed for use in the field. The author hopes to discuss this problem in a later paper.

The work of many authors (see, for example, Mitsui, 1955) associates the levels of nitrogen in waterlogged soils with its state of reduction. Partly subjective observations by the present author support this and tend to show that the fertility of a given paddy soil is largely defined by its level and rate of supply of available nitrogen. It can thus be argued that the fertility of a paddy soil is dependent, in part at least, on its level and rate of reduction of ferric iron. Work in these laboratories tends to show that the Bremner and Shaw method is suitable for estimating available nitrogen in waterlogged soils; it would be particularly useful if it would also serve as a means of testing their state of reduction.

Kontobi 5 soil, which is very low in iron, showed no increase in Fe^{II} extracted with time after submergence and there is no change in the soil pH. On the other hand, Rokupr 1 soil, high in iron, showed a steady increase in extracted Fe^{II} and its pH increased by about one unit. Also, in agreement with Bradfield (1941) cited by Ponnamperuma (1955), the BS extracts showed no subsidiary inflexions during the potentiometric titrations and their endpoints were equivalent to the Fe^{II} contents of the solutions. These results support the argument that ferric iron is the principal electron acceptor in a waterlogged soil, being reduced to ferrous ions which enter the soil solution. They also show that equation (1) is basically correct although it is quite possible that the presence of

organic complexing compounds (Bloomfield, 1952) might render it an over-simplification of the state of affairs.

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THE AVAILABLE-WATER CAPACITY OF A SANDY LOAM SOIL

I. A CRITICAL COMPARISON OF METHODS OF DETERMINING THE MOISTURE CONTENT OF SOIL AT FIELD CAPACITY AND AT THE PERMANENT WILTING PERCENTAGE

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Summary

To assess the effects of cultural and manurial treatments on the available-water capacity of a sandy loam soil it was necessary to determine the upper and lower limits of the available water.

The results of determining the moisture content of the soil at field capacity (FC) by two methods have been compared. It has been found that the direct method involving soil sampling after irrigation and when drainage had almost ceased, gave more accurate and consistent results than the suction-plate method using any single tension.

With the soil which had received farmyard manure, the permanent wilting percentage (PWP) determined on undisturbed cores and on crushed samples of soil by the sunflower technique showed significant differences and for critical work the results of determinations made on soil cores were preferred. The desiccator method of determining PWP was found to be insufficiently accurate for use in this type of work.

Introduction

THE results of experiments at Wellesbourne have shown that applications of farmyard manure (FYM) significantly increased the yield of several vegetable crops (Haworth, 1959). Only a part of the increases in yield could be attributed to the nutrients supplied by the FYM, and hence it follows that other factors were involved. The better growth in dry weather of the plants on plots which had received FYM indicated that more water might be available to them than to the poorer plants on the no-FYM plots. There is a strongly held opinion amongst soil scientists and horticulturists that FYM and other bulky organic manures increase the water-holding capacity of a soil, but there is little published experimental work to support this opinion. Jamison (1956), in a review of the literature, concluded that any increase in the available-water capacity (AWC) of soil following applications of organic manures was so small, even on sandy soils, as to be of no practical value.

The assessment of the AWC of a soil depends on the accurate measurement of the upper limit, field capacity, and the lower limit, the permanent wilting percentage, of the available water of that soil. Veihmeyer and Hendrickson (1931) defined FC as the amount of water held in the soil after excess gravitational water had drained away and the rate of downward movement of water had materially decreased; and stated that, from the definition, the FC of a soil could be measured most accurately by soil sampling a few days after rain (Veihmeyer and Hendrickson,

1949). This direct method, however, is laborious and time-consuming and several laboratory techniques have been developed to determine FC from small samples of soil.

The wilting coefficient of Briggs and Shantz (1912), later termed the permanent wilting percentage (Hendrickson and Veihmeyer, 1929), was defined as the moisture content of a soil when the leaves of plants growing in the soil first reached a stage of wilting from which they did not recover when placed in a saturated atmosphere without the addition of water to the soil. Generally the PWP is determined on small samples of soil in the laboratory using sunflower plants to indicate when the soil has dried out to the PWP. Many indirect methods of determining the PWP of soils have been developed to replace the time-consuming sunflower test (e.g. Da Costa, 1938; Breazeale and McGeorge, 1949; and Lehane and Staple, 1951) but only the 15-atm. percentage determined with the pressure-membrane apparatus has been widely used.

The methods in general use for the determination of FC and PWP do not use soil in its field condition. The present work was carried out to find whether the discrepancy between informed opinion and the experimental evidence about the AWC of soils could be attributed to errors introduced into the measurements of FC and PWP either by using soil in an artificial condition or by arbitrary methods of assessment in the laboratory.

A comparison of different methods of determining FC and PWP was made on soil which had been subjected to different cultivation and manurial treatments in the above-mentioned experiments.

Field-capacity measurements were made using the direct and suction-plate methods, but the moisture equivalent of the soil, which has been widely used as an index of field capacity, was not determined since it was reported to be an unreliable measure of FC on coarse-textured soils (Veihmeyer and Hendrickson, 1931, 1949). Lehane and Staple's (1951) simple, indirect method of determining PWP based on the absorption of moisture by air-dried soil samples in an atmosphere of 99 per cent. relative humidity was compared with the standard sunflower method. In addition, the PWP was determined by the sunflower method on crushed samples and undisturbed cores of soil, for Veihmeyer and Hendrickson (1946, 1948) showed that for compacted soils the PWPs determined on disturbed samples of soil were meaningless when applied to field conditions. This paper deals with the differences between the results obtained by the different methods, and the importance of these differences in assessing the AWC of the experimental soils is discussed in Part II (Salter and Haworth, 1961).

Experimental Methods

The long-term cultivation experiment from which the soil samples were taken was started in 1953 and included the following primary cultivation treatments carried out for each crop; deep ploughing (14–16 in.), shallow ploughing (6–7 in.), shallow ploughing (6–7 in.) plus subsoiling (16–18 in.), and rotavating (6–7 in.). Each cultivation treatment was combined factorially with a manurial treatment in which either

FYM at 20 tons per acre per crop plus phosphate and potash or an inorganic nitrogen fertilizer without FYM, was given. The experiment was of a randomized block design with three phases and two replications of each treatment in each phase (Haworth, 1955). The soil was an alluvial sandy loam of the Newport series (Haworth, 1956).

Determinations of field capacity

(*a*) *Direct method.* An area of soil in each plot was irrigated with sufficient water on 13 July 1959 (7 weeks after the last experimental treatments had been carried out), to rewet the whole depth of soil to FC for Colman (1944) showed that the FC of field soils may depend on the depth of wetting. The area was covered to prevent evaporation and auger samples of soil were taken in duplicate from depths of 0–6, 6–12, 12–18 in. at 24-hour intervals up to 168 hours after irrigating, by which time downward movement of water had almost ceased. The moisture content of the samples was determined by drying to constant weight at 105° C.

(*b*) *Suction-plate method.* Undisturbed cores of soil were used for these determinations in order to minimize errors associated with the artificial soil structure which results from drying, sieving, and rewetting of the soil (Richards and Fireman, 1943, Smith, 1944, Veihmeyer and Hendrickson, 1946 and 1948; and Elrick and Tanner, 1955). The cores of soil were obtained by pushing metal cylinders horizontally into a vertical face of a trench dug across the irrigated area on 20 July 1959. The sampling cylinders were 2·4 in. in length and diameter and duplicate samples were taken at 3, 9, and 15 in. from the soil surface. After removal from the soil the ends of the cylinders were covered to prevent the soil from drying out.

In the laboratory both ends of the soil cores were trimmed and a layer of muslin was secured over one end of the cylinders with a rubber band. The cores were carefully saturated with water, and were placed on porous ceramic plates under a tension of 0·05 atm. until equilibrium was reached. The moisture content of the soil cores was then determined gravimetrically. A tension of 0·05 atm. was chosen since the results of FC determinations at this tension, using soil of the same type as that used in the main experiment but which had not been subjected to any of the experimental treatments, had shown close agreement with those obtained by the direct method. In addition to determining the moisture content at FC, the suction-plate method enabled the apparent specific gravity, the capillary and non-capillary pore space of the soil to be determined.

Determination of permanent wilting percentage

Sunflower methods (A and B). Cores of soil were taken as described for the suction-plate method of FC determination. One end of each cylinder was closed with a lid to make a container in which a sunflower plant could be grown. One half of the soil in each cylinder was removed and after crushing, a small sub-sample was withdrawn from it for use in method C (below).

The main part of the crushed soil was placed in a metal container similar to that which held the undisturbed soil. One sunflower seed was sown in each container of both undisturbed soil (method A) and disturbed soil (method B). The young seedling was watered until several pairs of leaves had formed and the roots had ramified throughout the soil sample; the soil surface was then covered to prevent direct evaporation of water from the soil and no further water was given to the plants. All except one pair of healthy leaves were removed to enable a more accurate assessment of the time of wilting to be made (Hendrickson and Veihmeyer, 1945). The plants were examined regularly and when wilting of the leaves occurred the plants were placed in a water-saturated atmosphere for 24 hours. If the leaves did not recover turgidity the soil was removed from the container, most of the roots were taken out and the moisture content of the soil was determined.

Desiccator method (C). The sub-sample of soil removed from each sampling cylinder was air dried. Lehane and Staple's (1951) method based on the absorption of moisture by soil samples in an atmosphere of 99 per cent. relative humidity was used to determine the PWP.

Results

Field-capacity determinations

The differences between the apparent soil moisture percentages at field capacity as determined by the two methods are given in Table 1.

TABLE 1

Differences in Soil Moisture Content at FC obtained by the Two Methods (Suction-plate Method minus Direct Method. Means of Four Determinations)

Mean sample depth (in.)	Deep ploughing		Shallow ploughing		Shallow ploughing + sub-soiling		Rotavating		Means		General mean
	FYM		FYM		FYM		FYM		FYM		
	−	+	−	+	−	+	−	+	−	+	
3	1·5	0·4	0·3	1·4	−0·7	−0·6	0·2	−1·4	0·4	−0·1	0·1
9	0·9	0·1	1·0	−0·6	1·0	0·2	0·7	−0·6	0·9	−0·2	0·3
15	−1·0	−1·0	2·3	0·5	1·0	−0·9	2·2	−2·0	1·1	−0·8	0·1
Mean .	0·5	−0·1	1·2	0·4	0·4	−0·5	1·0	−1·3	0·8	−0·4	0·2

The general mean of the suction-plate method was 13·5 and the direct method 13·3. To compare the values in the table with zero:

s.e. for values within the body of the table at 3″ and 9″ depths = ±0·46 (14 d. f.)
s.e. for values within the body of the table at 15″ depth = ±0·72 (7)
s.e. for column means = ±0·31 (23)
s.e. for general mean of − and + FYM treatment = ±0·16 (23)

The soil moisture percentages at field capacity as determined by the two methods are plotted against each other in Fig. 1. For soils which had received FYM for 6 years, the suction-plate method gave values for the soil moisture percentage at FC which were, in general, lower than those given by the direct method whereas for soils where FYM had not been

applied, the suction-plate method gave values which were, in general, higher than those given by the direct method. The mean difference between the results of the two methods for the + FYM series of soils was −0·4 and for the −FYM series of soils it was 0·8; both of these mean differences were statistically significant from zero and together are sufficiently large to be of importance in the assessment of the available water in the experimentally treated soils (Salter and Haworth, 1961).

The standard error per reading associated with the direct method (4·0 per cent. of the general mean) was lower than that associated with the suction-plate method (6·9 per cent. of the general mean).

Permanent Wilting Percentage Determinations

The differences between the PWPs determined on disturbed soil and undisturbed cores by the sunflower technique (methods A and B) are

TABLE 2

Differences in Permanent Wilting Percentage obtained by the Two Sunflower Methods (Crushed Soil minus Undisturbed Soil Method. Means of Four Determinations)

Mean sample depth (in.)	Deep ploughing		Shallow ploughing		Shallow ploughing + subsoiling		Rotavating		Means		General mean
	FYM		FYM		FYM		FYM		FYM		
	−	+	−	+	−	+	−	+	−	+	
3	−0·1	0·4	0·7	1·2	2·1	0·3•	0·0	−0·2	0·7	0·4	0·5
9	0·4	−0·3	0·2	0·5	1·0	0·5•	−0·4	−0·9	0·3	−0·1	0·1
15	1·7•	−0·2	−0·9	−0·6	−0·3	−0·4	1·8	2·0†	0·6	0·2	0·4
Mean . .	0·7	0·0	0·0	0·4	0·9	0·1	0·5	0·3	0·5	0·2	0·3

The general means of the disturbed and undisturbed soil methods were 6·0 and 5·7 respectively. To compare the values in the table with zero:

s.e. for values within the body of the table at 3″ depth = ±0·40 (7 d. f.)
s.e. for values within the body of the table at 9″ and 15″ depth = ±0·69 (13)
s.e. for column means = ±0·46 (199)
s.e. for general mean of − and + FYM treatment = ±0·23 (199)

• Figures include a single substituted plot value (1 out of 4) calculated by the method of Cochran and Cox (1950). The value was substituted because the determined value was grossly in error as a result of soil irregularities.

† Figure includes three substituted plot values (3 out of 4).

given in Table 2. These differences do not show any consistent trends with the cultivation treatments, but the mean differences of 0·5 for soil samples from plots which had not received FYM is statistically significant when $P = 0{\cdot}05$. The overall mean difference of 0·3 just fails to reach significance when $P = 0{\cdot}05$. The standard errors per reading, 20·3 and 14·1 per cent. of the mean for methods A and B respectively, are much higher than the corresponding errors for the determination of field capacity.

The desiccator method C gave values for the PWPs which were significantly higher than those given by either of the sunflower methods.

The differences in the PWPs as determined by method C and A are given in Table 3.

TABLE 3

Differences in Permanent Wilting Percentage obtained by the Sunflower Method and Desiccator Method (C minus A). (Means of Four Determinations)

Mean sample depth (in.)	Deep ploughing		Shallow ploughing		Shallow ploughing + subsoiling		Rotavating		Means		General mean
	FYM		FYM		FYM		FYM		FYM		
	−	+	−	+	−	+	−	+	−	+	
3	1·8	2·4	1·8	2·9	3·8	2·7	2·0	1·1	2·3	2·3	2·3
9	2·5	3·4	2·2	3·1	3·0	3·8•	3·0	0·8•	2·7	2·8	2·7
15	6·6•	2·6	5·2	2·8	3·6	2·6	3·7	6·4†	4·8	3·6	4·2
Mean . .	3·6	2·8	3·1	2·9	3·5	3·0	2·9	2·8	3·3	2·9	3·1

The general means of the undisturbed soil and the desiccator method were 5·7 and 8·8 respectively. To compare the values in the table with zero:

s.e. for values within the body of the table at 3″ depth = ±0·47 (7 d.f.)
s.e. for values within the body of the table at 9″ and 15″ depth = ±1·13 (13)
s.e. for columns totals = ±0·46 (199)
s.e. for general mean of − and + FYM treatment = ±0·23 (199)

• Figures include a single substituted plot value.
† Figure includes three substituted plot values.

Although the values as measured by the desiccator method showed relative differences in the effects of the cultivation and FYM treatments on the PWP of the soil, the absolute moisture percentages were not sufficiently close to the values determined by the sunflower methods to be worthy of further consideration in the present study.

Discussion

Although the sampling of soil after heavy rain or irrigation is by definition part of the standard method of determining the FC of a soil, many workers have estimated FC by equilibrating the moisture in a soil sample with a given tension using suction-plate or pressure-membrane apparatus. Their work has shown that when any single tension is used for a wide range of soils, an accurate estimate of FC cannot be expected since the tension corresponding to FC varies from soil to soil (Jamison, 1956). Colman (1947) showed that this tension increased as the moisture content of the soil at FC increased. Nevertheless, he suggested that a tension of 0·33 atm. could be used for the indirect determination of FC on most soils and Jamison and Kroth (1958) have also used 0·33 atm. on a large number of soils; other workers have used different tensions with satisfactory results, for example, Hanks, Holmes, and Tanner (1954) used 0·20 atm.; Haise, Haas, and Jensen (1955), 0·10 atm.; and Russell and Balcerek (1944), 0·05 atm. Results from previous determinations of FC on the soil used in the present work had indicated that 0·05 atm. was the tension likely to give the closest approximation to FC. The general

mean soil moisture content at FC obtained by the direct method was 13·3 per cent. and for the indirect method was 13·5 per cent., but it has now been shown that the experimental cultivations and FYM treatments had influenced the FC of the soils to such an extent that the use of the same tension for all the soils from the experimental plots was not justified (Fig. 1). If the correct tension had to be determined beforehand for each of the experimental soils in order to get an accurate estimate of FC by the suction-plate method the whole purpose of the

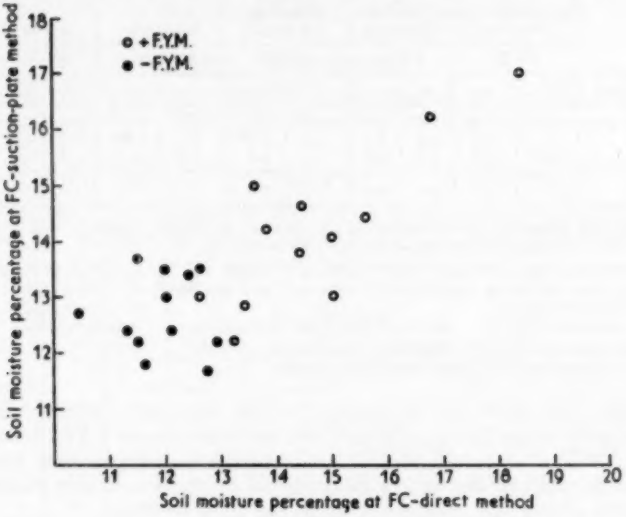

FIG. 1.

indirect method, i.e. speed of the determination, would be lost. Further it is not easy to determine quickly the correct tension to apply, for the soil moisture tension at FC, measured under natural conditions with a tensiometer, may not be the same as that required in the laboratory to obtain an accurate estimate of FC (Smith and Browning, 1947; and Richards and Wadleigh, 1952).

The present comparative study of the direct and an indirect method of determining FC has shown that where a rough estimate of soil moisture content at FC was required, the suction-plate method using undisturbed cores of soil gave satisfactory results, but for more critical work, the use of the direct sampling method was essential. This conclusion is in agreement with that of Marshall (1959), who, in a recent review, has stated that '. . . no laboratory method can be a real substitute for a field capacity measurement which is necessarily influenced by many other factors including especially the physical properties and initial moisture conditions of the profile as a whole'.

The results of PWPs determined by the three methods showed that the desiccator method of Lehane and Staple (1951) gave higher PWPs

than the direct sunflower methods. The consistently higher PWPs obtained cannot be explained by an error in the standard soil factor used in this method. Since an accurate determination of PWP was required and the differences between the values obtained by the desiccator and sunflower methods could not be satisfactorily explained, the desiccator method was not considered to be suitable.

The use of sunflowers as indicator plants for the direct determination of PWP in the laboratory has been regarded as the standard method even though the 15 atm. percentage is now commonly used. Several factors which may influence the determination of PWP using this technique have been reported (Furr and Reeve, 1945; Hendrickson and Veihmeyer, 1945). Veihmeyer and Hendrickson (1946, 1948) found that PWPs determined on fragmented samples obtained from a dense soil were meaningless when applied to natural conditions. The soil used in the present study was extremely dense in its undisturbed state with a high apparent specific gravity (Salter and Haworth, 1961), and it is therefore surprising, in view of Veihmeyer and Hendrickson's results, that larger differences in PWP were not found when undisturbed cores and crushed soil samples were compared. Although the cores of soil had a high density the sunflower roots had ramified extensively through them by the time the test was made. It should also be noted that most of the roots were removed from the soil before the moisture content was determined. In view of the accuracy required to determine the effects of experimental treatments on the PWP of this soil and the significant differences between the PWPs obtained by the two sunflower methods from plots receiving FYM, the values determined on the cores of undisturbed soil, i.e. closely approaching the natural state, were considered to represent the lower limit of available water.

The effects of cultivation and FYM treatments on the field capacity, permanent wilting percentage, apparent specific gravity and available water of this soil are discussed in a further paper (Salter and Haworth, 1961).

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THE AVAILABLE-WATER CAPACITY OF A SANDY LOAM SOIL

II. THE EFFECTS OF FARMYARD MANURE AND DIFFERENT PRIMARY CULTIVATIONS

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Summary

The effects of annual application of farmyard manure and of different cultivation treatments for a 6-year period on the available-water capacity of a sandy loam soil have been measured. It has been shown that the farmyard manure applications have led to a significant increase in the available-water capacity of the soil. The cultivation treatments influenced the available-water capacity to a lesser extent.

It is suggested that the reason why many previous workers have failed to detect an increase in available-water capacity in comparable experiments is that they did not use sufficiently accurate methods for the determination of field capacity and the permanent wilting percentage, i.e. the upper and lower limits of the available water in the soil.

Introduction

It has been reported by a number of workers that for most soils there was no significant increase in available-water capacity (AWC) following the incorporation of organic manures. However, in the majority of these investigations the upper limit of available water in the soil, field capacity, was measured at a suction of 0·33 atm. and the lower limit, the permanent wilting percentage, at 15·0 atm. (e.g. Jamison, 1953) despite known errors associated with these methods of determination.

The present investigation has been concerned with the effects of applications of farmyard manure (FYM), and to a smaller extent cultivation treatments, for a period of 6 years on the AWC of a sandy loam soil. The four primary cultivation treatments which were carried out for each crop were: deep ploughing (14–16 in.), shallow ploughing (6–7 in.), shallow ploughing (6–7 in.) plus subsoiling (16–18 in.), and rotavating (6–7 in.). Each cultivation treatment was combined factorially with a manurial treatment in which either FYM at 20 tons per acre per crop (a total of 160 tons per acre in the 6-year period) plus phosphate and potash, or an inorganic nitrogenous fertilizer without FYM, was given. The experiment was of a randomized block design with two blocks and three phases. The three phases permitted each crop of the rotation to be observed each year.

Salter and Haworth (1961) have shown that it was essential to use accurate methods of determining field capacity (FC) and the permanent wilting point (PWP) for any critical work on the assessment of available water of soils. In the present paper it has been shown that, using such methods, the addition of FYM to the soil significantly increased the AWC of a sandy loam soil.

Experimental Methods

The experimental treatments applied to the soil and the methods of determining FC and PWP have been described in a previous paper (Salter and Haworth, 1961). The direct sampling method, and the sunflower method using undisturbed cores of soil, were used for the determination of FC and PWP respectively.

The apparent specific gravity was determined by drying cylinders of undisturbed soil cores of known volume at 105° C. The available water capacity of the soil to a depth of 18 in. was calculated by the method of Israelson (1952).

The organic carbon content of the soils, sampled before the experimental treatments had started and again at the end of the 6-year period, was determined by the Walkley-Black method (1934).

Results

Field capacity

The soil moisture percentages at FC for all treatments and at three depths are given in Table 1. Farmyard manure increased the soil

TABLE 1

Effect of the Experimental Treatments on the Soil Moisture Content (%) *at Field Capacity* (*Means of Four Determinations*)

	Deep ploughing		*Shallow ploughing*		*Shallow ploughing + subsoiling*		*Rotavating*		*Means*		*General mean*
	FYM		*FYM*		*FYM*		*FYM*		*FYM*		
	−	+	−	+	−	+	−	+	−	+	
Depth 3″	12·0	13·8	12·1	13·6	12·9	16·8	11·6	18·4	12·1	15·6	13·9
9″	12·6	14·5	11·3	13·4	12·4	15·3	11·5	14·4	12·0	14·4	13·2
15″	12·7	13·2	10·4	12·6	12·0	15·0	11·5	15·0	11·7	13·9	12·8
Means .	12·4	13·8	11·3	13·2	12·4	15·7	11·5	15·9	11·9	14·7	13·3

s.e. for comparisons in the body of the table = ±0·39 (23 d.f.)
s.e. for comparisons of column means = ±0·22 (23)
s.e. for comparisons of row means = ±0·14 (23)

moisture content at FC with all the cultivation treatments and at all sample depths. The effect was more pronounced at the shallower depths. In the absence of FYM, the soil moisture content at FC following deep cultivation (deep ploughing or shallow ploughing plus subsoiling) was greater than that following shallow cultivation (shallow ploughing or rotavating).

Permanent wilting percentage

The PWPs of the soil are given in Table 2. The experimental treatments, both cultivation and FYM, had no consistent effect on the PWP of the soil. There was a trend for the PWPs to decrease with depth.

TABLE 2

Effect of the Experimental Treatments on the Permanent Wilting Percentage of the Soil (Means of Four Determinations)

	Deep ploughing		*Shallow ploughing*		*Shallow ploughing + subsoiling*		*Rotavating*		*Means*		*General mean*
	FYM		*FYM*		*FYM*		*FYM*		*FYM*		
	−	+	−	+	−	+	−	+	−	+	
Depth 3″	6·5	5·7	5·4	5·3	3·8	7·0	5·7	7·1	5·4	6·3	5·8
9″	5·9	5·5	5·2	5·3	5·2	6·5•	5·7	6·6	5·5	6·0	5·7
15″	5·3•	4·8	7·3	5·8	4·6	6·1	3·7	5·9•	5·2	5·7	5·5
Means .	5·9	5·3	6·0	5·5	4·5	6·5	5·0	6·5	5·4	6·0	5·7

s.e. for comparisons in the body of the table = ±0·81 (23 d.f.)
s.e. for comparisons of columns means = ±0·47 (23)
s.e. for comparisons of row means = ±0·29 (23)

• Figures include substituted plot values calculated by the method of Cochran and Cox (1950). The values were substituted because the determined values were grossly in error because of soil irregularities.

Apparent specific gravity

The apparent specific gravity (ASG) results are shown in Table 3. The application of FYM to the soil lowered the ASG except perhaps at the lowest depth sampled and the general mean of 1·70 for +FYM is significantly lower than that of 1·77 for −FYM. In the presence of FYM the ASG after the shallow cultivations was significantly lower than after the deep cultivations which is understandable since FYM was concentrated in the shallow layers of soil. In the absence of FYM the ASG of the soil after shallow ploughing plus subsoiling was significantly lower than after the other treatments, whilst after rotavation it was significantly higher than after deep ploughing, or shallow ploughing plus subsoiling.

TABLE 3

Effect of the Experimental Treatments on the Apparent Specific Gravity of the Soil (Means of Four Determinations)

	Deep ploughing		*Shallow ploughing*		*Shallow ploughing + subsoiling*		*Rotavating*		*Means*		*General mean*
	FYM		*FYM*		*FYM*		*FYM*		*FYM*		
	−	+	−	+	−	+	−	+	−	+	
Depth 3″	1·85	1·69	1·77	1·63	1·69	1·68	1·86	1·67	1·79	1·67	1·73
9″	1·82	1·81	1·86	1·68	1·83	1·78	1·89	1·65	1·85	1·73	1·79
15″	1·63	1·88	1·70	1·60	1·67	1·67	1·67	1·67	1·67	1·71	1·69
Means .	1·77	1·79	1·78	1·64	1·73	1·71	1·81	1·66	1·77	1·70	1·74

s.e. for comparisons of depths for same treatment in body of table = ±0·079 (18 d.f.)
s.e. for comparisons between treatments at same depth in body of table = ±0·066 (16)
s.e. for comparisons of column means = ±0·015 (16)
s.e. for comparisons of row means = ±0·028 (7)

Available-water capacity

The effect of the various treatments on the AWC of the top 18 in. of soil is shown in Table 4. With each cultivation treatment and at each depth sampled, FYM increased the amount of available water held in the soil. FYM increased the amount of available water in the top 18 in. of soil by about 33 per cent. with deep ploughing, shallow ploughing, and rotavating, but only 15 per cent. with shallow ploughing plus subsoiling. One of the largest increases in AWC, almost 75 per cent., was found in the top 6 in. of soil where the application of FYM was combined with rotavation but the increase in AWC in the corresponding horizon in the soil of the shallow ploughing treatment, again in presence of FYM, was only 12 per cent.

TABLE 4

Effect of the Experimental Treatments on the Available-Water Capacity of the Soil (inches)

	Deep ploughing		*Shallow ploughing*		*Shallow ploughing + subsoiling*		*Rotavating*		*Means*		*General mean*
	FYM		*FYM*		*FYM*		*FYM*		*FYM*		
	−	+	−	+	−	+	−	+	−	+	
Depth 0–6″	0·60	0·82	0·72	0·81	0·92	0·99	0·65	1·13	0·72	0·94	0·83
6–12″	0·74	0·97	0·68	0·82	0·79	0·93	0·66	0·77	0·72	0·87	0·80
12–18″	0·72	0·95	0·31	0·65	0·74	0·89	0·78	0·91	0·64	0·85	0·74
Totals .	2·06	2·74	1·71	2·28	2·45	2·81	2·09	2·81	2·08	2·66	2·37

s.e. for comparisons between treatments at same depth in body of the table = ±0·082 (15 d.f.)
s.e. for comparisons between depths of same treatment in body of the table = ±0·060 (16)
s.e. for comparisons of row means = ±0·030 (16)
s.e. for comparisons of column totals = ±0·139 (7)

The AWC of the soil was lower after shallow ploughing than after the other three cultivation treatments, significantly so in the presence of FYM but not in its absence. In the absence of FYM the AWC was significantly higher after shallow ploughing plus subsoiling, than after the other cultivation treatments.

TABLE 5

Effect of the Experimental Treatments on the Organic Carbon Percentage of the Soil (Means of Two Determinations)

	Deep ploughing		*Shallow ploughing*		*Shallow ploughing + subsoiling*		*Rotavating*		*Means*		*General mean*
	FYM		*FYM*		*FYM*		*FYM*		*FYM*		
	−	+	−	+	−	+	−	+	−	+	
Depth 0–6″	0·68	0·82	0·68	0·94	0·73	0·94	0·74	1·20	0·71	0·98	0·84
6–12″	0·70	0·88	0·58	0·70	0·62	0·88	0·68	0·68	0·64	0·78	0·71
Mean .	0·68	0·85	0·64	0·82	0·67	0·91	0·71	0·94	0·68	0·88	0·78

s.e. for comparisons in the body of the table = ±0·057 (15 d.f.)
s.e. for comparisons of column means = ±0·041 (15)
s.e. for comparison of general mean of FYM treatments = ±0·020 (15)

Carbon content of the soils

The carbon content of soil samples taken from the plots in 1953 before the experimental treatments were begun was 0·79 and 0·66 per cent. for the 0–6 in. and 6–12 in. depths respectively. The plots were resampled in 1959 and the carbon contents of the soils from the various treatments are shown in Table 5. It will be seen that FYM significantly increased the carbon content of the soil with all cultivation treatments

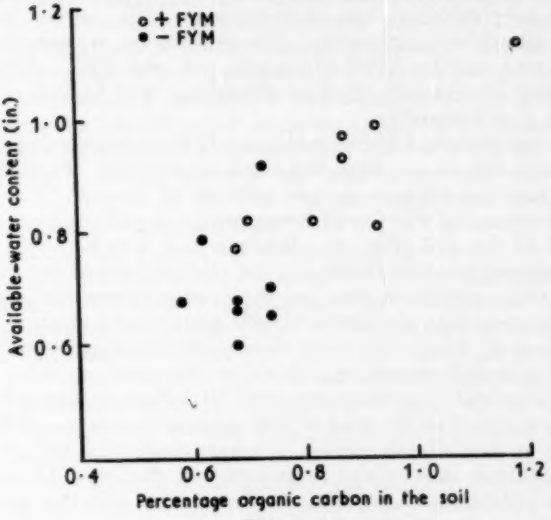

FIG. 1

and at both depths excepting at the 6–12 in. depth of the rotavating treatment.

In the presence of FYM the AWC increased with increasing carbon content but in soil where no FYM had been applied there was no such relationship (Fig. 1).

Discussion

Increased yields of crops have often been reported following the application of farmyard manure (FYM) to the soil and it has been generally believed that the increase in yield may be partially caused by a higher available-water content of the soil. However, many workers have failed to detect any increase in the AWC of soils which had received regular applications of FYM, often over long periods of time. Consistent improvement in the AWC from organic matter additions has usually been obtained only in coarse textured soils. Jamison (1953) showed that, except for sandy soils, organic matter increases did not increase the capacity of a soil to store available water. Even the increase in AWC in sandy soils was stated to be so small in relation to amount of organic matter increase as to be of no practical value (Jamison, 1956).

In the present work it has been shown that the AWC of the top 18 in. of a sandy loam soil has been significantly increased by up to 33 per cent. by the application of FYM over a period of 6 years. As would be expected the cultivation treatment influenced the effect of the FYM on the AWC of the soil since the depth of incorporation of the FYM varied with the cultivation treatment. The greatest increase in AWC in any one soil horizon occurred where the FYM was incorporated in the surface 6 in. by rotavation. It is noteworthy in this respect that with shallow cultivation there was an increase in AWC on the +FYM plots *below* the depth of cultivation. The cultivation treatments also were found to influence the AWC of the soil, the total AWC of the top 18 in. of soil being lowest with shallow ploughing and highest with shallow ploughing plus subsoiling.

The incorporation of FYM in this sandy loam containing about 53 per cent. coarse sand, 28 per cent. fine sand, 10 per cent. silt, and 8 per cent. of clay raised the organic carbon content of the soil (Table 5) and a general relationship was found between the organic carbon content and the AWC of the soil (Fig. 1). Jamison and Kroth (1958) found that AWC increased generally with organic matter content but because they found that the organic matter increased with coarse silt and decreased with clay content they attributed the effect to textural changes. Heinenon (1954), however, found the main beneficial effects of organic matter on AWC to be in soils containing about 30 per cent. or more of the clay fraction. Marshall (1959) has suggested that these opposing views can be reconciled in terms of the state of the organic matter under the different conditions in the following way: 'Jamison dealt with soils to which the organic materials were added as in tillage operations. Heinenon's soils were undisturbed under pasture. In the pasture soils the organic matter is more intimately associated with the soil particles and Heinenon considers that it apparently improves the porous structure of the aggregates so that there are more pores of the right size for holding available water.'

The results presented in this paper show that the AWC of the soil at Wellesbourne has been altered primarily through the effect of the experimental treatments on the FC of the soil. The application of FYM increased the FC of the soil (Table 1) but the effect of this increase in FC on the AWC was partly counteracted by a reduction in apparent specific gravity (Table 3) and a non-significant increase in moisture content at the PWP (Table 2). Nevertheless, the increase in the FC of soil which had received FYM was large enough to increase the AWC to a significant extent.

The results also show that it is a matter of prime importance to determine the moisture content of the soil at FC as accurately as possible when critical comparisons of the AWC of soils are being made.

The hyperbolic nature of the soil moisture characteristic curve emphasizes the importance of determining the moisture content at FC accurately; a small difference in tension when the soil is approximately at FC can make a large difference to the moisture content of the soil. Salter and Haworth (1961) have shown that when a tension of 0·05 atm. was used to determine FC indirectly, the soil moisture contents differed

significantly from those obtained from the direct determination of FC even though the mean difference between the indirect and direct methods was only 0·2 per cent. Although these differences in moisture content at FC were comparatively small, the use of the FCs, determined indirectly, to calculate AWC resulted in a reduction of the actual difference between the FYM treatment means of 0·58 in. (Table 4) to 0·21 in. Furthermore, preliminary work on the moisture characteristic curves of the soils receiving the FYM treatments has shown that at 0·33 atm. suction the difference in soil moisture content between the +FYM and −FYM soils were only one-quarter of those found at the true FC. Thus the use of the 0·33 atm. percentage as a measure of FC in the present experiment would have considerably reduced, if not eliminated, the difference in AWC between the experimental treatments. However, many workers have accepted 0·33 atm. as the standard suction at which to determine the FC of soils in the laboratory, not only to compare the effects of experimental treatments on the FC of a given soil but also to compare FCs of soils of different composition.

Of fourteen relevant papers reporting the effects of organic matter on the moisture characteristics and AWC of soils, only one worker, Heinenon (1954), used the direct sampling method of determining FC. In eight of these papers the moisture equivalent was used as an approximation to FC (Feustel and Byers, 1936; Coile, 1939; Bertramson and Rhodes, 1939; Bouyoucos, 1939; Salter and Schollenberger, 1939; Havis, 1943; Klute and Jacob, 1950; and Russel, Klute, and Jacob, 1952): in those reported in four later papers the 0·33 atm. percentage was used (Jamison, 1953; Gingrich and Stauffer, 1955; Jamison and Kroth, 1958; and Bartelli and Peters, 1959); and in one investigation, 0·05 atm. was used (Russell and Balcerek, 1944). The PWP was determined by the standard sunflower method in only three experiments. In five papers the 15 atm. percentage was reported to have been used and the remaining workers used various other indirect methods of determining PWP.

It is concluded from the present study that the application of FYM annually for 6 years to a sandy loam soil increased the available water capacity of the soil. It is considered probable that the failure of previous workers to detect increases in the AWC of soils in comparable experiments was a failure of technique rather than an indication that no differences in AWC existed.

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AN INVESTIGATION OF THE PRESSURE-MEMBRANE METHOD FOR MEASURING THE SUCTION PROPERTIES OF SOIL

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Summary

Two new forms of pressure-membrane apparatus are described. One has been developed for routine use, while the other has been used for pressure-membrane tests at very high pressures (up to 1,500 atmospheres, or pF 6·2).

For soil in both the wetting and drying condition it is shown that the relation between suction and moisture content determined by pressure-membrane tests agrees with that obtained using the suction plate, the centrifuge, the vacuum desiccator, and the sorption balance. The rate of attainment of moisture equilibrium in the pressure membrane is also examined experimentally, for a very wide range of air pressures.

Introduction

THE relationships between the suction and moisture content for soils have a bearing upon the growth of plants, and also upon the behaviour of soil when used as a constructional material in civil engineering. Pressure-membrane technique is employed in both fields of study.

An element of soil *in situ* can be regarded as being acted upon by a total stress tensor, the principal total stresses being σ_1, σ_2, and σ_3, together with a pore water pressure u, a pore air pressure π, an osmotic pressure in the soil solution P, and a temperature θ. These seven quantities are defined to be measured directly, the zero for the first five being the pressure of the atmosphere, and are regarded as independent variables. Their value determines the magnitude of the four dependent variables, moisture content, volume per unit mass and shear strength of the soil, and the total free energy depression of the soil water.

The problem of expressing these factors in terms of the seven independent variables could be solved by direct experiment and a thermodynamic analysis, but some simplification is normally employed. The agricultural scientist is concerned mainly with the variables u and P, and regards the total free energy depression of the soil water as practically proportional to the sum $P-u$. In road and airfield engineering it has been the practice to reduce the independent variables to four, viz. the temperature θ, and three mean principal effective stresses, for moisture content, volume, and shear strength respectively defined by (Croney *et al.*, 1958, 1960)

$$S = (u-\pi)-\alpha(p-\pi) \tag{1}$$

$$\sigma'_v = (p-\pi)-\beta(u-\pi) \tag{2}$$

$$p' = \tfrac{1}{3}J'_1 = \sigma'_i = (p-\pi)-\beta'(u-\pi) \tag{3}$$

In this approach the osmotic pressure P has been ignored, and the

total stress tensor has been replaced by the first invariant, $J_1 = 3p$, equal to the sum of the principal total stresses. The coefficients α and β can be calculated from thermodynamic relationships if the soil behaves reversibly. If in addition the coefficients are sensibly constant, then (1) and (2) are true exactly, otherwise they are approximations. Equation (3) may be written in terms of the suction S, from (1), to give:

$$\tfrac{1}{3}J_1' = -\beta' . S + (\tfrac{1}{3}J_1 - \pi)(1 - \alpha . \beta'), \qquad (3a)$$

an equation relevant to the study of yield and failure criteria of soil, Coleman (1960).

If the soil is saturated, whether u is positive or negative, all the effective stresses, eqs. (1), (2), and (3), are equal numerically to the single variable $p-u$, a simplification of the general problem that has been much used in the soil mechanics of deep foundations.

In spite of the many limitations, equation (1) has been used successfully to predict the moisture distribution in shallow foundations where u is usually negative and the soil saturated or unsaturated (Black *et al.*, 1958; Russam, 1959). The relationship between the suction S and the moisture content of the soil has formed an essential part of these studies, and the pressure membrane has proved to be a useful method for determining the relationship. In the method, $u = p - \pi = 0$ when the soil is in equilibrium and so equation (1) becomes $S = -\pi$.

Three forms of pressure-membrane apparatus have been developed at the Road Research Laboratory for use in studies in moisture distribution. A large machine to accommodate samples of soil of up to 5 in. by 6 in. is limited to values of S up to 500 lb. per sq. in. A machine for routine use, to accommodate soil specimens up to 2 in. by 2 in. is limited to values of S up to 2,000 lb. per sq. in. (pF 5·3). A third machine, to take specimens of soil only 1 cm. by 1 cm. is limited to values of S up to 22,000 lb. per sq. in. (pF 6·2). The machines are all now available commercially, and the second and third are described in this paper (see also Croney *et al.*, 1952, 1958, and 1960).

The suction S is normally defined to include both the hydrostatic component u and the osmotic component P of the total free energy depression of the soil water (Schofield, 1935). The suction and pressure plate, pressure membrane, oedometer, and centrifuge methods measure only the hydrostatic component u of the suction S. The vacuum desiccator, sorption balance, and freezing-point depression methods measure the total free energy depression which is almost proportional to $P-u$. Comparisons of the methods have been made by Schofield (1935), using the vacuum desiccator, centrifuge, freezing-point, and suction plate, Russell (1939), Richards and Fireman (1943) using the pressure plate and suction plate, and Collis-George (1955) using the suction plate, pressure membrane, and vacuum desiccator, while earlier unpublished studies at the Road Research Laboratory established equivalence between the vacuum desiccator and the sorption balance. In this paper the three methods used by Collis-George are employed, together with the sorption balance and centrifuge, a large overlap between the pressure membrane and the methods based upon vapour pressure being obtained.

Origins of the pressure-membrane method. The pressure membrane was preceded by experiments on ultrafiltration carried out by McBain and his collaborators (1928, 1933, 1936). Solutions of large molecules and colloids such as 'ferric hydroxide' (Rooksby, 1951) soap and sugars were forced through membranes of collodion or cellophane by pressure. Partial separation of the solute from the solvent was obtained in this way, the solution that had passed through the membrane being of lower concentration than before filtration. The pressure membrane for soil was at first used in a similar way, to isolate the soil solution for analysis, by Reitemeier and Richards (1944).

Development of experimental technique. Conventional ultrafiltration equipment was first applied to soil by Woodruff (1940), and shortly afterwards Richards (1941) designed and constructed the first apparatus specifically for use with soil.

Richards's equipment consisted of two large metal disks bolted to, and sealing, the ends of a short length of metal tube of large bore. The membranes used in this first apparatus were supported on wire gauze, and consisted of cellophane sheet of between 0·9 and 1·7 thousandths of an inch in thickness. Alternatively, commercial Zsigmondy 'Ultrafein' filters were used. Air pressures up to 16 atmospheres were employed and the apparatus produced up to 6×10^{-6} c.c. of soil solution per atmosphere pressure per second. A novel feature employed was a rubber sheet above the specimen of soil, and held in the upper seal. This could be made to press the soil into contact with the membrane, by the application of a higher air pressure above the sheet than that surrounding the sample of soil.

The major advance in experimental technique subsequent to this early work has been the use of the Visking plastic membrane in place of cellophane. This membrane is a cellulose product, and the sheeting first used by Reitemeier and Richards (1944) was 4 thousandths of an inch in thickness. The Visking membrane, which is available in a range of thicknesses, has been used in almost all subsequent work and has been shown to be very suitable. With its aid, Richards (1949) has been able to measure moisture retention in soils up to 105 atmospheres (pF 5·04). Richards states that in unpublished studies he has managed to obtain measurements at 180 atmospheres (pF 5·27) but that the membrane may leak above 110 atmospheres. In Great Britain Collis-George (1955) has recently published membrane measurements on a pure montmorillonite at pressures up to 150 atmospheres (pF 5·20).

Subsidiary advances in technique have included a range of devices for controlling the air pressure automatically at a fixed value (Richards, 1947 and 1949). Richards and Weaver (1944) have also shown that there is a steady diffusion of gas through the membrane which in one case was $1{\cdot}3 \times 10^{-6}$ c.c. per sq. cm. per second per unit atmosphere pressure. Nitrogen gas was used in this instance. Its use helps to minimize rusting of the pressure chamber, which is likely to impair the membrane. The use of nitrogen in place of air pressure also reduces the possibility of explosions.

The pressure-membrane apparatus is now patented in the United

States (Richards, 1944) and is available commercially there. The applications of the method have so far been almost entirely in the field of agriculture, for which it was developed (see Woodruff, 1940; Richards, 1941, 1948, 1956; Richards and Weaver, 1943 and 1944; Gardner, 1956; Collis-George, 1955). A detailed review of this work is given in an unpublished report from the Road Research Laboratory.[1]

Objects of the Present Investigations

The objects of the present work were:

1. To develop a pressure-membrane apparatus for routine work to cover the range of the centrifuge method and provide an alternative to that method.
2. To develop an apparatus for research purposes to cover a much wider range of suctions than had previously been attempted, the purpose being to study in detail the continuity of the relation between suction and moisture content.
3. To investigate the use of the pressure-membrane apparatus for studying the relation between suction and moisture content for soils in the wetting condition. Previous work with the method had been largely confined to drying tests.
4. To compare suction data obtained with the pressure membrane, suction plate, centrifuge, vacuum desiccator, and sorption balance.
5. To determine the time required for soil to reach moisture equilibrium in the pressure membrane at a range of suction values, for the soil in both the wetting and drying conditions.
6. To develop the pressure membrane as a rapid method for measuring the suction of soil samples as taken from the field.

Pressure-membrane Apparatus for Routine Testing

A form of pressure-membrane apparatus suitable for routine laboratory studies of the relation between suction and moisture content within the range 0·1 to 100 atmospheres (pF 2 to pF 5) has been developed. A diagram of the equipment is shown in Fig. 1.

Frame and pressure vessel. The steel yoke and base plate form a quick-release device in which the brass pressure vessel is normally held. The pressure vessel is 4 in. in external diameter, and is in two halves. The upper half is fitted with a pressure gauge and a fine adjustment needle valve of the normal gas cylinder type. The lower half contains the porous bronze disk, membrane and two water outflow pipes which are connected to the water reservoirs by transparent polythene tubing. The rubber ring seal is mounted in a groove in the lower face of the top half of the pressure vessel, and presses on the membrane at its outer edge. Springs on each vertical pillar of the steel yoke ensure that the top beam of the yoke does not fall when the pressure vessel is removed.

To remove the pressure vessel, the air is released from the needle valve, and the 1-in. Whitworth nuts on the vertical pillars are released very slightly (about one-quarter of a turn). The pressure vessel can then

[1] RN/3464/JDC obtainable by application to the Director of Road Research.

be withdrawn sideways from the yoke, and opened to reveal the soil sample. Using this arrangement the equipment can be made to operate at pressures up to 2,000 lb. per sq. in. and yet be dismantled in about 20 seconds. Large box spanners are used to turn the nuts on the vertical pillars, but no tommy bars need be employed. Moderate hand tightness has been found to be adequate to secure freedom from air leaks.

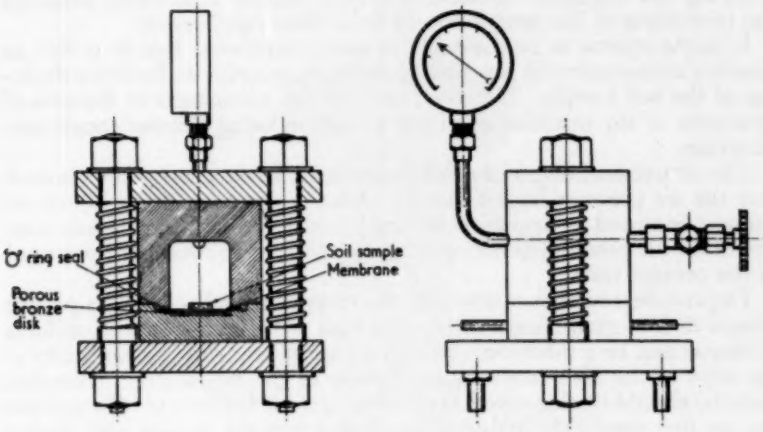

FIG. 1. Diagram of pressure-membrane apparatus.

Pressure gauges and air supply. A range of interchangeable pressure gauges can be fitted to the apparatus. Ranges of 0–50, 0–200, 0–500 and 0–2,000 lb. per sq. in. have been found to be suitable. It is desirable that the pressure should be measured to an accuracy of about 2 per cent. so that the corresponding pF values can be obtained to about 0·01 units on the pF scale.

In the present work compressed air from a gas cylinder was used to fill the pressure vessel. For routine work nitrogen would be preferable to reduce corrosion. In either case the maximum pressure available is 2,000 lb. per sq. in. from a fresh cylinder. This is equal to 136 atmospheres, the corresponding pF obtained in the machine being 5·15. The apparatus is made to accept this pressure safely.

The air seal. The air seal used is a synthetic rubber 'O' ring of 0·139-in. diameter section. It is held in a groove of 2¼-in. diameter in the pressure vessel. A groove depth of 0·090 in. has been found to be suitable so that about two-thirds of the ring is immersed in the groove.

Membrane material. The cellulose membrane (Stamm, 1956) used in the present work is about 0·004 in. in thickness in the air-dry condition. On placing the membrane in water it assumes a moisture content (based on the air-dry weight) of about 70 per cent., and expands in thickness to about 0·007 in. This expansion of thickness, which is complete in about 50 seconds, is accompanied by anisotropic expansion in the direction of

the sheet, a circular piece of the air-dry material assuming an elliptical shape after wetting.

Normally the membrane is placed wet in the apparatus and conditioned for a few minutes at the desired air pressure before placing the soil sample on it. This precaution is necessary in wetting tests since, if the sample becomes too wet accidentally, the ultimate moisture content may be too high owing to the hysteresis in the suction/moisture content relation. In a drying test the final moisture content would be unaffected, although the re-wetting of the sample would delay final equilibrium.

It might appear to be desirable to use a membrane that is as thin as possible consistent with mechanical strength, in order to facilitate drainage of the soil sample. However, no material advantages in the rate of operation of the machine has been found on using thinner membrane materials.

The air permeability of the membrane used in the present tests is such that the air pressure vessel falls by about 2 per cent. in 24 hours, an amount regarded as negligible by the present authors. Automatic control of the air pressure is not envisaged at present and has not been used in the present tests.

To provide mechanical strength, the membrane is backed by a porous bronze disk of grade A porosity. The disk must be flat and of uniform thickness and be a flush close fit in the base plate. Any discontinuity at the edge of the disk could cause rupture of the membrane. The disk material should be degreased in ether or acetone before use. To remove any air that passes through the membrane into the porous disk during a test, vacuum can be applied to either of the water reservoirs. Initial saturation of the porous plate by boiling in distilled water is advisable.

Size of soil sample. Soil samples of 2 in. in height by 2 in. in diameter can be accommodated in the apparatus described. In all the work discussed in the present paper small soil samples about $\frac{1}{8}$ in. in height were employed to accelerate the testing programme.

With the membrane materials at present available in Great Britain a machine with a plate diameter of 7 in. could be constructed. This means that 6-in. diameter samples could be accommodated in a suitable pressure vessel. A machine of this size has in fact been developed and is now in routine use at the Road Research Laboratory.

Tests with thicker samples of clay soil using the larger type of machine suggest that the time for drainage of samples of clay soil 3–4 in. thick might be 1–2 months, and rather less for lighter soils.

Pressure-membrane Apparatus for Very High Pressure

In the present experiments it was desired to study the continuity of the relation between suction and moisture content and to compare as far as possible results from the pressure membrane with those obtained using other methods such as the vacuum desiccator and sorption balance. The apparatus described above, being designed for a maximum pressure of 2,000 lb. per sq. in., gave a maximum suction in the soil of pF 5·15, below which value the two methods based on vapour pressure measurements are not very reliable. A special apparatus was therefore built to

extend the pressure membrane data as far as practicable into the vapour pressure range. A diagram of the equipment is shown in Fig. 2. Pressures up to 21,500 lb. per sq. in. can be developed in the apparatus corresponding to a suction of pF 6·18.

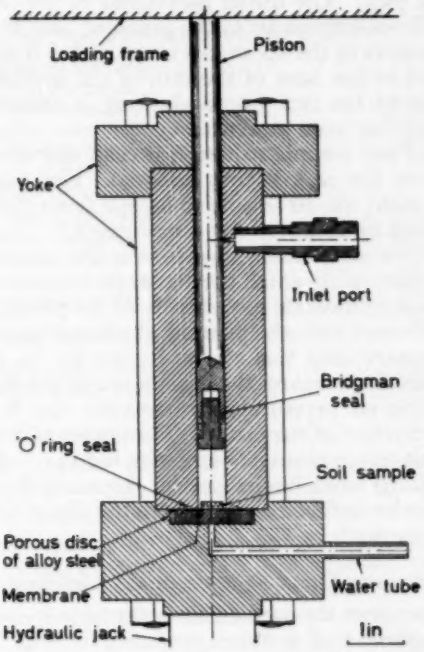

FIG. 2. Membrane apparatus for high pressure.

The apparatus consists of a brass cylinder of 2 in. external diameter having an axial circular bore of ½-in. diameter provided with an inlet port near one end capable of being connected to a supply of compressed air. A brass piston fitted with a free 'mushroom' head of the Bridgman type (Bridgman, 1931), and incorporating a sliding rubber seal, is free to move in the cylinder. A yoke, consisting of two brass end-pieces held together by four steel threaded rods and nuts of ½ in. diameter, is fitted across the ends of the cylinder. The lower end-piece contains a disk of sintered nickel chrome steel (connected as in the apparatus already described to a supply of water at atmospheric pressure), the cellulose membrane and a small synthetic rubber 'O' ring as an air seal.

The equipment is mounted in a loading frame capable of accepting an axial load of up to 5 tons and is supported in the frame by a calibrated hydraulic jack also of 5 tons maximum load fitted with an oil pressure gauge and a ram of known diameter. To conduct a test, the apparatus is

assembled with the sample of soil adhering to the membrane. The piston is then inserted through the upper end-piece into the end of the bore above the inlet port and the equipment set up on the jack in the loading frame. Compressed air at a pressure of about 2,000 lb. per sq. in. is then introduced into the inlet port, and the pressure intensified by operation of the hydraulic jack. The initial movement of the piston cuts off the inlet port and allows surplus air in the pressure hose to escape above the piston. The pressure in the apparatus is computed from the area ratio of the cylinder bore to the bore of the ram of the hydraulic jack, and the pressure reading on the jack gauge. Jacking is discontinued when the required pressure has been attained.

To remove the soil sample to weigh it each day or at the end of the test, the valve on the jack is first released. The gas pressure forces the piston back until the air is able to escape from the inlet port. The apparatus can then be removed for dismantling.

Preliminary tests were made to estimate the piston friction, which affected the accuracy with which the actual pressure could be estimated. Using a dial gauge to indicate movements of the piston, the oil pressure was noted in each case with the piston just advancing and just receding. The highest pressure used was 21,490 lb. per sq. in. corresponding to pF 6·18. For this air pressure, the maximum oil pressure was 1,870 lb. per sq. in. Of this oil pressure approximately 120 lb. per sq. in. was absorbed by the friction of the piston. The observed density of the compressed air, about 0·6 g. per c.c., corresponded to a volume about three times that computed from Boyles law for the pressure used, so that the pressure could not be deduced directly from the observed volume changes of the air.

Relation between pF and Pressure in the Membrane Apparatus

The relation between the applied air pressure π lb. per sq. in. and the hydrostatic component of suction produced in soil moisture by the membrane apparatus, when the soil has reached moisture equilibrium and has been removed from the apparatus can be shown to be

$$\mathrm{pF} = 1{\cdot}8477 + \log_{10} \pi, \qquad (4)$$

the constant 1·8477 being the logarithm of the factor for converting from lb. per sq. in. to cm. of water. This equation has been used to deduce all the experimental results, and to make all the calculations, given in this paper.

Experimental Results

The soil used in most of the experimental work was a Gault clay from Shaves Wood, Sussex. The liquid limit was 107 per cent., the plastic limit was 33 per cent., and the clay content 60 per cent. The natural moisture content was about 50 per cent. (on a dry weight basis), although some variability was observed. The apparent specific surface of the clay for water sorption deduced by the B.E.T. method was about 200 sq. m. per g., based on the sorption data given later in this paper. This figure suggests that up to one-half of the clay fraction of the soil might consist

of the clay mineral montmorillonite, a conclusion in harmony with the X-ray analysis of the soil. Earlier work (Lewis, 1950) has shown that existing roads founded on this Gault clay have been subject to considerable seasonal variations in level.

The following tests were carried out on the soil in the conditions and by the methods given below:

1. *Natural soil drying from zero suction to oven dryness*

Suction plate tests in the range	pF 1–pF 3
Centrifuge tests in the range	pF 3·7–pF 4·1
Pressure membrane tests in the range	pF 2·5–pF 6·2
Vacuum desiccator tests in the range	pF 5–pF 7
Sorption balance tests in the range	pF 5–pF 7

2. *Soil wetting from oven dryness to zero suction*

Suction plate tests in the range	pF 1–pF 3
Centrifuge tests in the range	pF 3·8–pF 4·0
Pressure membrane tests in the range	pF 2·3–pF 5·0
Vacuum desiccator tests in the range	pF 5–pF 7
Sorption balance tests in the range	pF 5–pF 7

3. *Soil in the continuously disturbed condition*

'Rapid' flow tube tests in the range	pF 1–pF 3
Pressure membrane tests in the range	pF 3–pF 4·5

4. *Soil wetting- and drying-rate tests*

In each of the pressure membrane tests the samples of soil were weighed each day to determine the rate of drying in the drying tests, and the rate of wetting in the wetting tests.

A few additional tests were carried out to determine whether the pressure membrane could be used as a 'rapid' method for measuring the suction of soil samples taken straight from the field, &c. For this a sandy clay soil from Harmondsworth, Middlesex, was used.

The results of all the suction tests detailed in items 1, 2, and 3 are shown in Fig. 3. The tests on disturbed soil, item 3, are shown on a large scale in Fig. 4.

The rate of drying of the samples of soil in the drying tests, items 1 and 4 in the above list, are shown in Figs. 5 and 6. The rate of wetting of the soil in the wetting tests, items 2 and 4, are shown in Fig. 7.

The results of the 'rapid' membrane tests on Harmondsworth sandy clay are shown in Fig. 8.

Discussion of Experimental Results

Drying tests. The results of the drying tests shown in Fig. 3 (upper curve) show that there is good general agreement between the results obtained by the five different methods where they overlap, bearing in mind that different samples from the same core were used for each determination. In particular, there is no evidence of any systematic difference between the pressure membrane, centrifuge and suction plate data as might be expected. In addition, the pressure-membrane data are in good agreement with the results from the sorption balance particularly

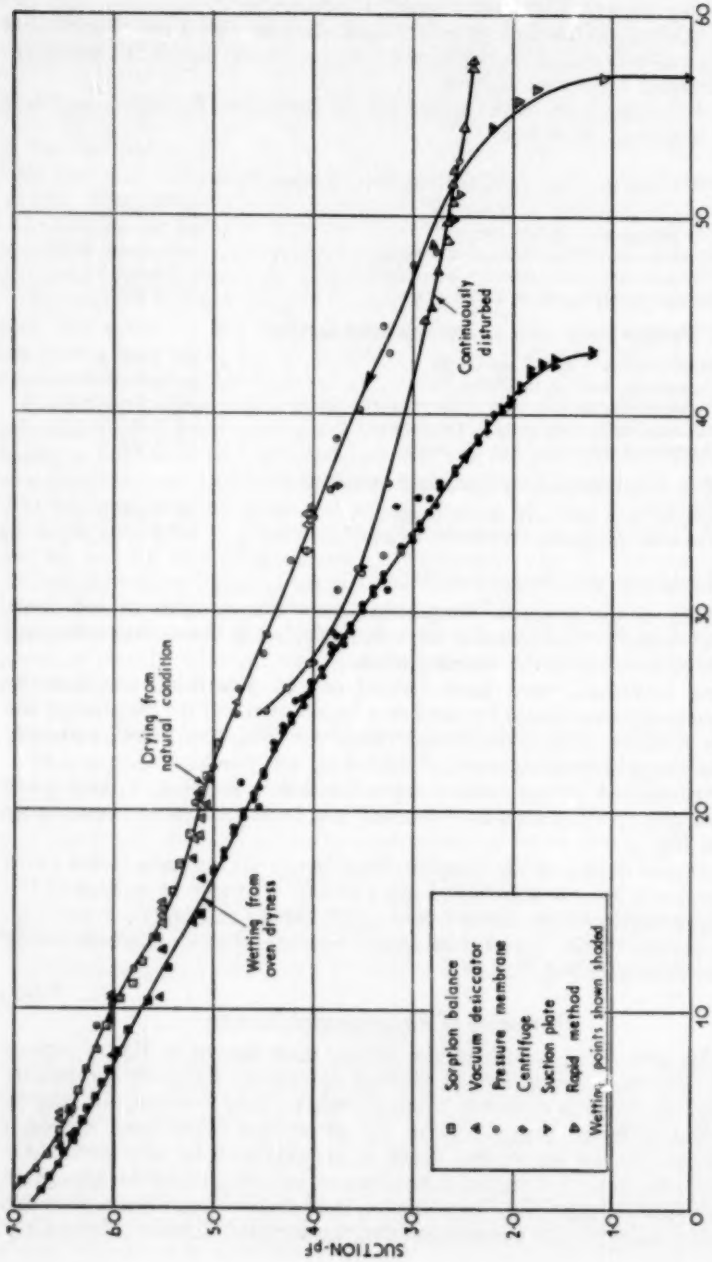

FIG. 3. Suction/moisture content relationship for Gault Clay.

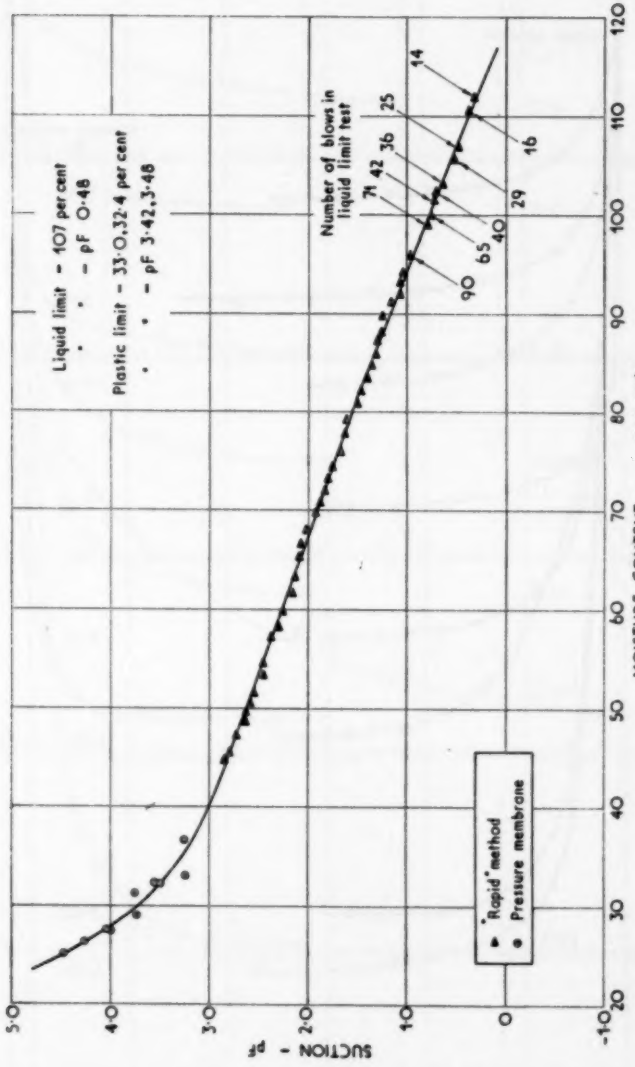

FIG. 4. Suction/moisture content relation for continuously disturbed Gault Clay.

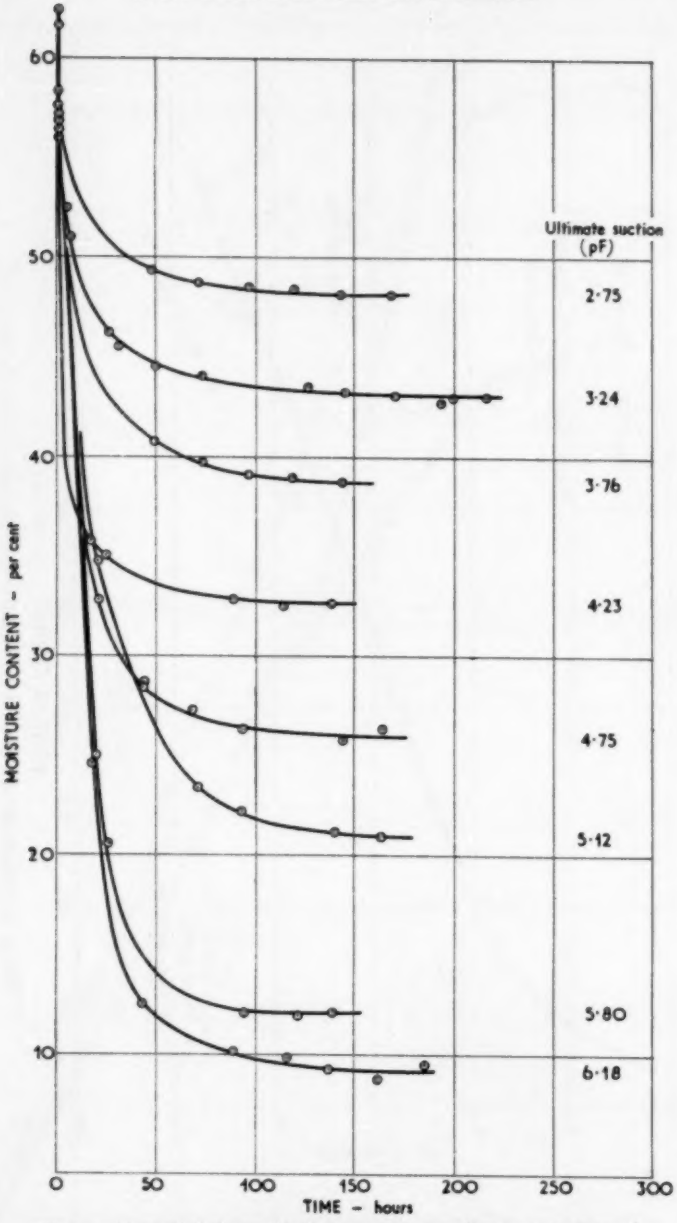

FIG. 5. Rate of drainage in the pressure-membrane apparatus of samples of Gault Clay initially at zero suction.

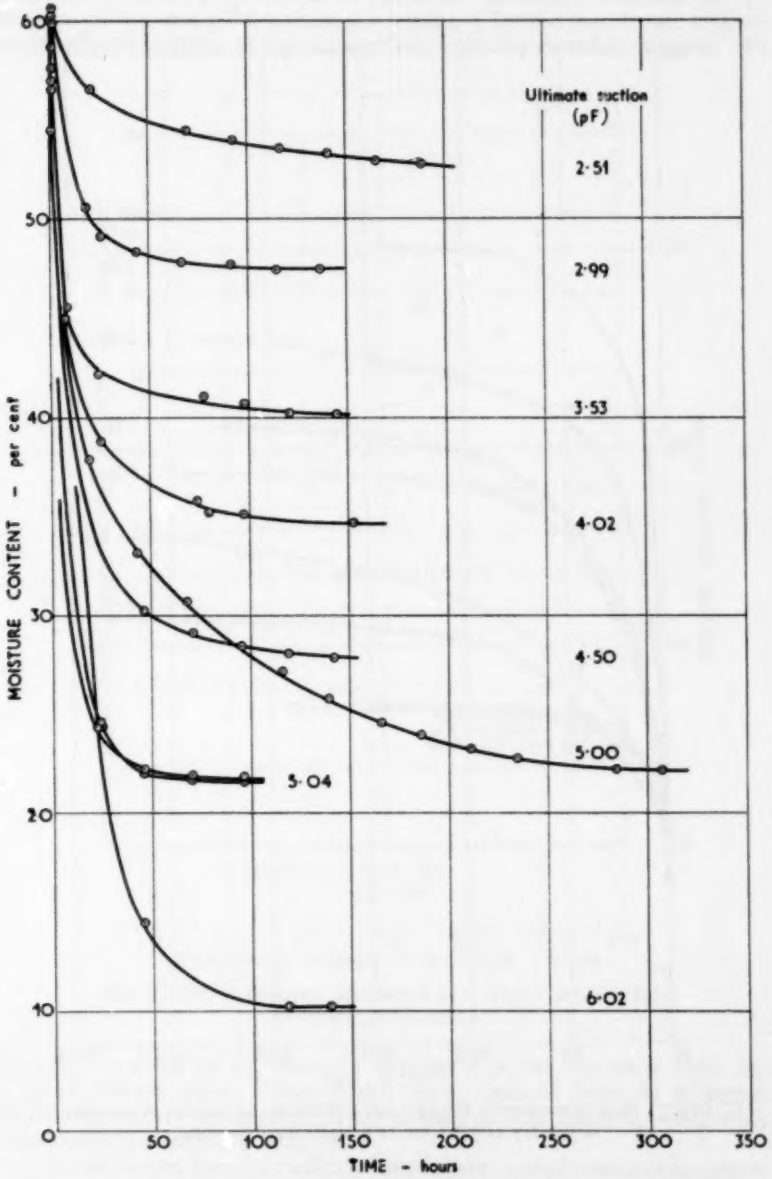

FIG. 6. Rate of drainage in the pressure-membrane apparatus of samples of Gault Clay initially at zero suction.

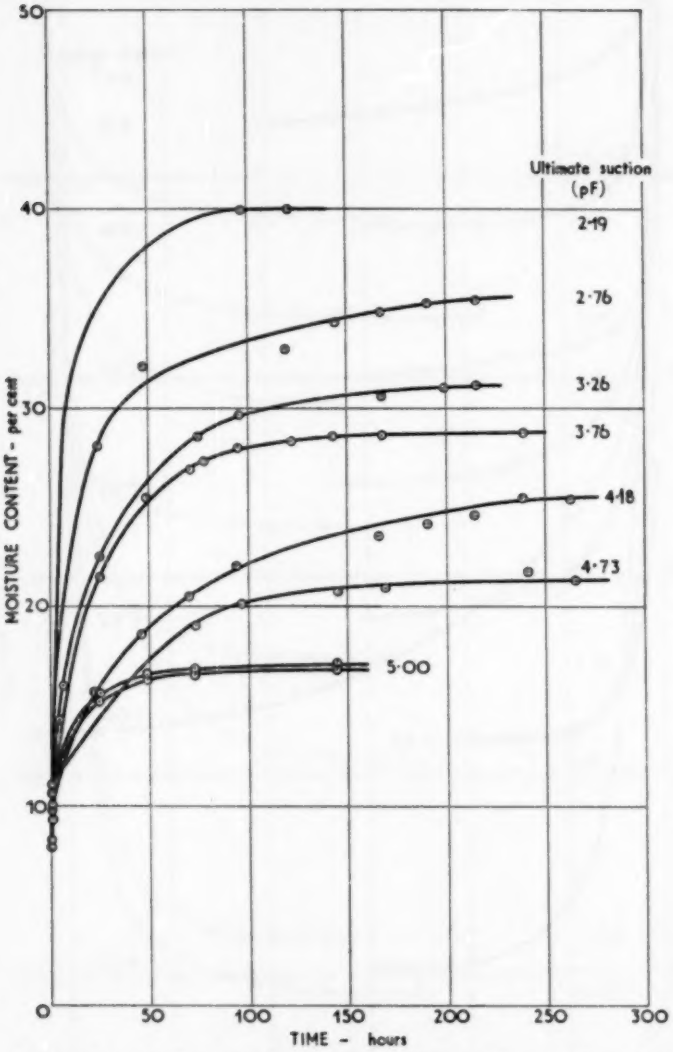

FIG. 7. Rate of wetting in the pressure-membrane apparatus of samples of air-dry Gault Clay at various final suctions.

at the lower end of the range of the latter method, i.e. about pF 5. Between pF 5·1 and pF 6·2 there is a tendency for the membrane to give results slightly wetter, at a given suction, than the sorption balance. At

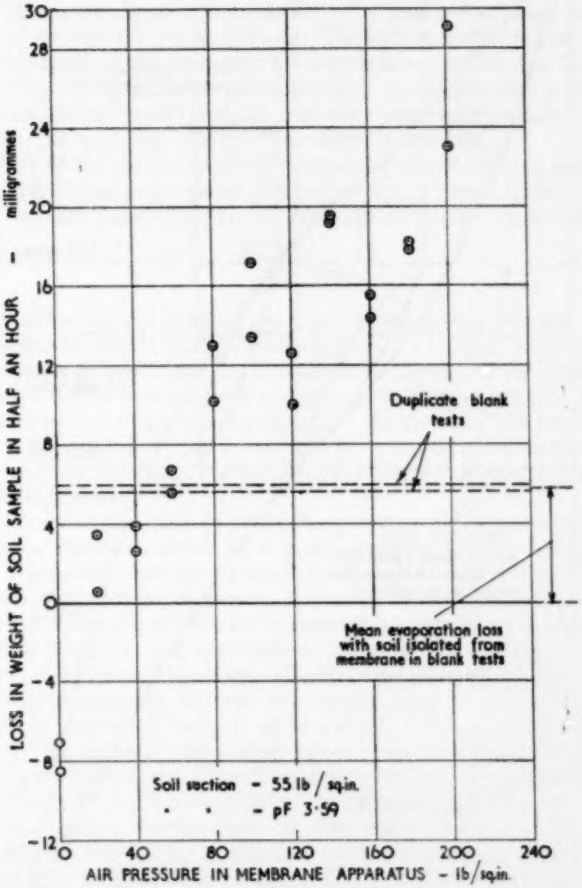

FIG. 8. Use of pressure membrane as a 'rapid' method for measuring soil suction.

about pF 5 some of the vacuum desiccator points are drier than the sorption balance data. These points were obtained from an unlagged desiccator, points obtained from a well-lagged desiccator agreeing with those from the sorption balance.

It is well known that the methods based upon vapour pressure measurement are inaccurate at, and below, pF 5 unless good control of temperature is available (Croney *et al.*; Owen, 1952). The effect of temperature

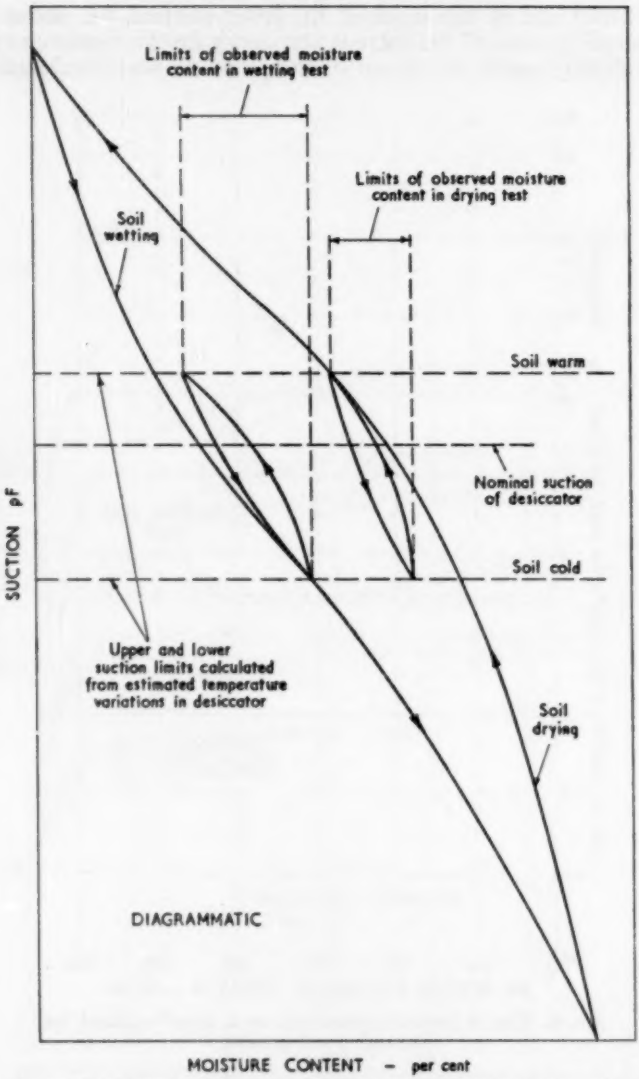
Limits of observed moisture content in wetting test
Limits of observed moisture content in drying test
Soil wetting
Soil warm
Nominal suction of desiccator
Soil cold
Upper and lower suction limits calculated from estimated temperature variations in desiccator
Soil drying
DIAGRAMMATIC
SUCTION pF
MOISTURE CONTENT – per cent

FIG. 9. Effect of temperature fluctuations on the final moisture content observed in the vacuum desiccator test.

fluctuation is to make drying points too dry, and wetting points too wet, Fig. 9. The results given here suggest that the sorption balance may be rather less prone to such errors than the vacuum desiccator under normal circumstances. This result is expected, excessive evaporation

from the sample in the sorption balance giving rise to a correcting back pressure absent in the desiccator.

A critical point is the small discrepancy observed between the membrane data and the methods based upon vapour pressure. The effect, whatever the cause, is absent at about pF 5 and below, and appears in the range of suction pF 5·1 and above. The fact that the vapour-pressure methods measure total free energy depression, while the membrane measures only the hydrostatic component (if the membrane is permeable to salts in solution) would suggest that the membrane points should be, if anything, too dry. In fact they are slightly too wet.

The effect of the air pressure in the membrane apparatus is threefold. The pressure in the pore water of a soil sample is raised, the density of the water is raised, and the vapour pressure of the water is raised. The equation

$$\pi = \frac{R.\theta.\rho}{M} \log_e \frac{H}{100} \qquad (5)$$

which describes approximately the latter effect is well known, where H is the relative humidity at a plane surface of pure water subject to a gas pressure π, at temperature θ. Calculation shows, using data for the volume of water in tension and compression, Barkas (1949), Bridgman (1931), that errors in the density of water can cause errors amounting to 0·01 units of pF at pF 5·7, 0·02 units at pF 6·0, and 0·03 units at pF 6·2. These errors are, however, too small and of the wrong sign to explain the observed discrepancy.

It follows from equation (5) that the pressure membrane employs the same vapour pressure ratio at a given suction as the direct vapour-pressure methods (vacuum desiccator, &c.), but in the opposite sense. Distillation of moisture, however, seems to be an unlikely cause of the discrepancy, since the effects are absent at low suction values (pF 5).

A further possible, and speculative, cause of the discrepancy may be the enhanced density of the water affecting the geometry of the soil/water system, thus making the soil too 'dry' under pressure. On this basis, the soil might be expected to take up too much water at a given nominal suction, by an amount depending upon both the enhanced density of water and also the suction characteristics of the soil. This approach would suggest that at pF 6·2 the membrane results would be about 0·5 per cent. of moisture content wetter than the data based upon vapour pressure, a conclusion in reasonable agreement with the observed facts.

Wetting tests. The results of the wetting tests shown in Fig. 3 (lower curve) indicate agreement between the results obtained by the five different methods. The possible sources of error are the same as those for the drying results and the data support the same broad conclusions.

Tests on soil in the 'continuously disturbed' condition. The suction/moisture content results for the soil in the fully disturbed condition are shown in Fig. 3 (middle curve). Results for London clay and Harmondsworth silty clay in this condition together with a description of the techniques used have already been published for the suction range pF 0 to 3·5 (Croney and Coleman, 1954). Both the liquid

limit and the plastic limit for the soil are represented by points on this curve.

The continuously disturbed curve is shown in more detail in Fig. 4. The 'rapid' technique employing a suction plate, capillary flow tube, and adjustable manometer were employed to obtain suction data up to pF 3·0 on soil originally slurried and subsequently allowed to dry slowly with continuous disturbance. The pressure-membrane points were obtained as for a drying test, but the sample was fully disturbed by hand after being weighed each day. It was found that the soil became too hard and brittle to disturb in this way at about pF 4·5, and this suction represents the upper limit of the disturbed curve. No direct comparison of the membrane data and the 'rapid' flow tube data was attempted, but the combined results define a continuous curve.

It has not hitherto been possible to obtain the continuously disturbed curve in a satisfactory manner at suction values in excess of pF 3·0, although by extrapolation of the rapid method using flow rates it was found that the suction of London Clay (from Heathrow) was about pF 3·4 at the plastic limit (Croney and Coleman, 1954). The suction at the liquid limit was pF 0·8. The corresponding suctions for the Gault Clay were found to be pF 3·45 and pF 0·48, Fig. 4. The mean of duplicate values of the moisture content at the plastic limit was used in conjunction with the disturbed curve to find the value of suction corresponding to the plastic limit. At the higher moisture contents liquid-limit tests were conducted on the slurried soil and the number of blows required to close the gap was measured in the usual way, Fig. 4. The suction of the soil when 25 blows were required was taken as the suction corresponding to the liquid limit.

The suction at which the disturbed curve cuts the curve for the soil in the drying condition, Fig. 3, was found to be pF 2·6. The corresponding suction for the London Clay already referred to was pF 3·4, the two curves for this soil intersecting at the plastic limit, apparently by coincidence.

An unexpected feature of the curve for the continuously disturbed soil, Fig. 3, is that it passes closer to the wetting curve for the natural soil than to the drying curve. This result is rather surprising because the soil in the disturbed condition would be expected to have a very disorganized structure, whereas in the soil wetting from oven dryness a comparatively compact structure created by the intense consolidation pressure, associated with the oven drying process, would be anticipated.

Soil wetting- and drying-rate tests. The rate of drying of soil samples in the pressure-membrane apparatus is shown in Figs. 5 and 6. About 150 hours is required for equilibrium to be obtained, independent of the final suction in the pF range 2·5 to 6·2.

The wetting tests, Fig. 7, require about 200–250 hours to complete. Substantial reductions in the time required could be expected if the soil examples could be made to adhere more perfectly to the membrane, by making the lower surface of the soil flatter. The effect of poor contact on the equilibrium time is shown by a test carried out at a suction of pF 5, Fig. 6.

Use of the Pressure Membrane as a 'Rapid' Method

It is frequently desired to measure the suction of the moisture in a given sample of soil. The moisture content of the soil during such a measurement must remain sensibly constant in order that the suction to be measured shall not vary. The measurement must therefore be made quickly to avoid losses of moisture from the soil by evaporation, and the method must not involve significant changes in the moisture content of the soil. Rapid methods have therefore been devised to effect such measurements.

A rapid method using a suction plate connected to a capillary tube and a variable suction head has already been described (Croney, Coleman, and Bridge, 1952). This method was used to obtain the suction data on disturbed soil shown in Fig. 4 within the pF range from zero to 3·0. Suitable suction plates cannot be obtained to extend this method above pF 3·0.

An attempt was made to use the pressure membrane as a rapid method in the pF range 3·0 upwards. The results are shown in Fig. 8.

The soil used was sandy clay. It was compacted in a B.S. standard compaction mould at about 1 per cent. of moisture content dry of the optimum. Soil samples of $\frac{3}{4}$ in. in diameter by $\frac{1}{8}$ in. in height were prepared using a suitable cutter, and the end of the soil was made as flat as possible. The samples were placed at a fixed gas pressure in the membrane apparatus for $\frac{1}{2}$ hour. They were weighed before and after the test and the change in weight recorded. Duplicate soil samples were tested at a range of gas pressures, fresh samples being cut for each different pressure. Two 'blank' tests were also carried out with the soil isolated from the membrane in order to assess the evaporation loss during the weighing process, &c.

A roughly linear relation was shown between the loss of weight and the pressure of gas, Fig. 8. Two horizontal lines drawn on the graph and displaced upwards from the line of zero weight-change are also shown. The displacements are equal to the loss of weight in $\frac{1}{2}$ hour found in the two blank tests. A weight loss by the soil equal to the mean of that observed in the blank tests was observed at a membrane pressure of about 55 lb. per sq. in. This value is taken as equal to the suction of the soil.

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